Environment Canada
Environmental Protection Service

Environnement Canada
Service de la protection de l'environnement

ENVIRO
**T**echnical
**I**nformation for
**P**roblem
**S**pills

# SULPHURIC ACID and OLEUM

February 1984

Canada

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## ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

# SULPHURIC ACID AND OLEUM

## ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
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## FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

## ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The Canadian Chemical Producers' Association is especially acknowledged for its review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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# 1 SUMMARY

## SULPHURIC ACID ($H_2SO_4$)

Colourless, odourless oily liquid

## SYNONYMS

Battery Acid, Fertilizer Acid, Oil of Vitriol, Hydrogen Sulphate, Sulphuric Acid spent, Acide Sulphurique (Fr.)

## IDENTIFICATION NUMBERS

UN No. Acid: 1830, Spent Acid: 1832; CAS No. Acid: 7664-93-9; OHM-TADS No. 7216915; STCC No. Acid: 4930040

## GRADES & PURITIES

Commercial Grade (66°Bé): >93.19 percent

Electrolytic - Battery Acid Grade: >93.19 percent

CP (Chemically Pure) Grade: 95.5-96.5 percent

## IMMEDIATE CONCERNS

Fire: Not flammable or combustible. Hydrogen gas may be formed on contact with metal

Human Health: Acid mists and liquid are corrosive to tissues, by inhalation and contact

Environment: Harmful to aquatic life in some species, in concentrations as low as 6 mg/L

## PHYSICAL PROPERTY DATA

| | 95.5-96.5% | 66°Bé |
|---|---|---|
| State (15°C, 1 atm): | liquid | liquid |
| Boiling Point: | 310°C | 279.4°C |
| Melting Point: | 3°C | -29.5°C |
| Flammability: | not flammable | not flammable |
| Specific Gravity (water=1): | 1.8437 | 1.8354 |
| Solubility (in water): | completely miscible, with evolution of heat | |
| Behaviour (in water): | sinks and reacts evolving heat | |
| Odour Threshold and Range: | low concentration is odourless; in fire, high concentration emits $SO_3$ with an odour threshold >1 mg/m$^3$ | |

## ENVIRONMENTAL CONCERNS

Harmful to aquatic life in low concentrations primarily due to its acidity. There is no potential for bioaccumulation or food chain concentration.

## HUMAN HEALTH

TLV*: 1 mg/m$^3$
IDLH: 80 mg/m$^3$

Exposure Effects

Inhalation: Mists and vapours are corrosive, causing damage to both the upper respiratory tract and the lungs. May cause coughing or sneezing

Contact: Rapidly damaging to all human tissues. Causes severe burns to skin and eyes, depending on concentration

## IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Call authorities and notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not flammable or combustible, but may form explosive hydrogen gas by reaction with metals. Dry chemical or carbon dioxide may be used to extinguish adjacent fires.

## COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill by diking with dry earth, sand, or other available material. Neutralize and remove material with pumps or vacuum equipment

Water: Contain with weirs, damming with gravel, earth, or by diversion. Neutralize and remove sludge

Air: Use water spray to knock down and disperse vapours. Control runoff for later treatment and/or disposal

## NAS HAZARD RATING

| Category | Rating |
|---|---|
| Fire | 0 |
| Health | |
| Vapour Irritant | 2 |
| Liquid or Solid Irritant | 4 |
| Poisons | 2 |
| Water Pollution | |
| Human Toxicity | 2 |
| Aquatic Toxicity | 3 |
| Aesthetic Effect | 2 |
| Reactivity | |
| Other Chemicals | 4 |
| Water | 3 |
| Self-reaction | 0 |

NFPA HAZARD CLASSIFICATION

## OLEUM ($H_2SO_4+SO_3$)

Colourless, oily liquid with a choking odour

## SYNONYMS

Fuming Sulphuric Acid, Disulphuric Acid, Dithionic Acid, Pyrosulphuric Acid

## IDENTIFICATION NUMBERS

UN No. Acid: 1831; CAS No. 8014-95-7; OHM-TADS No. 7216915; STCC No. 4930030

## GRADES & PURITIES

20 to 65 percent of excess $SO_3$

## IMMEDIATE CONCERNS

Fire: Not flammable and not combustible. Hydrogen gas formed by reaction of the acid with metal may accumulate inside tanks regardless of strength. Oleum is very reactive with many substances and reacts violently on contact with water

Human Health: Acid mists and liquid are corrosive to tissues, by inhalation and contact

Environment: Harmful to aquatic life in some species, in concentrations as low as 6 mg/L

## PHYSICAL PROPERTY DATA

| | Oleum by % excess $SO_3$ | | |
|---|---|---|---|
| | 30% | 25% | 20% |
| State (15°C, 1 atm): | liquid | liquid | liquid |
| Boiling Point: | 115°C | 125°C | 138°C |
| Melting Point: | 22°C | 14°C | 1°C |
| Flammability: | not flammable | not flammable | not flammable |
| Specific Gravity (water=1): | 1.952 | 1.935 | 1.916 |
| Solubility (in water): | completely miscible, with evolution of heat | | |
| Behaviour (in water): | sinks and mixes violently, evolving heat | | |
| Odour Threshold and Range: | >1 mg/m$^3$ | | |

## ENVIRONMENTAL CONCERNS

Harmful to aquatic life in low concentrations, primarily due to its acidity. There is no potential for bioaccumulation or food chain concentration.

## HUMAN HEALTH

TLV•: 1 mg/m$^3$
IDLH: 80 mg/m$^3$

Exposure Effects

Inhalation: Mists and vapours are corrosive, causing damage to both the upper respiratory tract and the lungs. May cause coughing or sneezing

Contact: Rapidly damaging to all human tissue. Causes severe burns to skin and eyes

## IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Call authorities and notify manufacturer. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not flammable or combustible, but may form explosive hydrogen gas by reaction with metals. Dry chemical or carbon dioxide may be used to extinguish adjacent fires.

## COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill by diking with dry earth, sand, or other available material. Neutralize and remove material with pumps or vacuum equipment

Water: Contain with weirs, damming with gravel, earth, or by diversion. Neutralize and remove sludge

Air: Use water spray to knock down and disperse vapours. Control runoff for later treatment and/or disposal

## NAS HAZARD RATING

| Category | Rating |
|---|---|
| Fire | 0 |
| Health | |
| Vapour Irritant | 2 |
| Liquid or Solid Irritant | 4 |
| Poisons | 2 |
| Water Pollution | |
| Human Toxicity | 2 |
| Aquatic Toxicity | 3 |
| Aesthetic Effect | 2 |
| Reactivity | |
| Other Chemicals | 4 |
| Water | 3 |
| Self-reaction | 0 |

NFPA HAZARD CLASSIFICATION

## 2 PHYSICAL AND CHEMICAL DATA

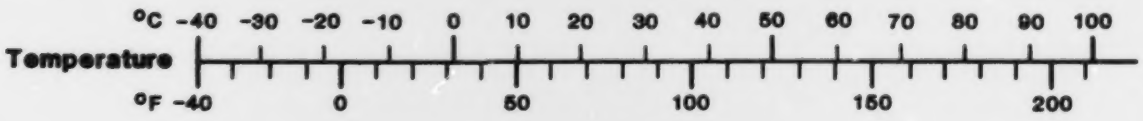
| | Sulphuric Acid | | Oleum | | |
|---|---|---|---|---|---|
| **Physical State Properties** | 95.5-96.5% | 66°Bé | 30% | 25% | 20% |
| Appearance | Colourless to amber, slightly cloudy, oily liquid (CIL) | | Colourless to white, heavy, oily liquid containing sulphur trioxide dissolved in sulphuric acid (CIL) | | |
| Usual shipping state(s) | Liquid (CIL) | | Liquid (CIL) | | |
| Physical state at 15°C, 1 atm | Liquid | | Liquid | | |
| Freezing point | 3.0°C (CRC 1980) | -29.5°C (CIL) | 22°C (CIL) | 14°C (CIL) | 1°C (CIL) |
| Boiling point | 310°C (CIL) | 279.4°C (Ashland MSDS 1977) | 115°C (Cities MSDS) | 125°C (CIL) | 138°C (Cities MSDS) |
| Decomposition temperature | 340°C (Merck 1976) | | | | |
| **Densities** | | | | | |
| Specific gravity (15°/15°C) | 1.8437 (CIL) | 1.8354 (CIL) | 1.952 (CIL) | 1.935 (CIL) | 1.916 (CIL) |
| **Fire Properties** | | | | | |
| Flammability | Not flammable (NFPA 1978) | | | | |
| Decomposition temperature | 340°C (Merck 1976) | | | | |
| Decomposition products | Sulphur oxides and water (Merck 1976) | | | | |
| **Other Properties** | | | | | |
| Molecular weight of pure substance | | 98.08 (CRC 1980) | | | |

| | Sulphuric Acid | | Oleum | | |
|---|---|---|---|---|---|
| | 95.5-96.5% | 66°Bé | 30% | 25% | 20% |
| Constitutent components of typical commercial grade | 95.5-96.5% $H_2SO_4$ (CCPA 1982) | 93.2% (min) $H_2SO_4$ (CIL) | 28.0 to 32.5% free $SO_3$ (CIL) | 22.7 to 27.2% free $SO_3$ (CIL) | 18.0 to 22.2% free $SO_3$ (CIL) |
| Refractive index | 1.437 (18°C) (CRC 1980) | | | | |
| Viscosity (est. 25°C) | 21 mPa•s (CIL) | 20 mPa•s (CIL) | 36 mPa•s (CIL) | 33 mPa•s (CIL) | 29 mPa•s (CIL) |
| Liquid interfacial tension with air | 55.1 mN/m (20°C) (CRC 1980) | | | | |
| Liquid interfacial tension with water | 75 mN/m (33 wt. % solution 25°C) (CRC 1980) | | | | |
| Hygroscopicity | Hygroscopic (MCA 1963) | | | | |
| Latent heat of fusion | 9.8 kJ/mole (at melting point) (CRC 1980) | | | | |
| Latent heat of vaporization | 56 kJ/mole (at boiling point) (JANAF 1971) | | | | |
| Heat of formation | -813.9 kJ/mole (25°C) (JANAF 1971) | | | | |
| Ionization potential | - | | 11.0 eV (as $SO_3^+$) (Rosenstock 1977) | | |
| Heat of solution | -971 J/g (CHRIS 1978) | | | | |
| Heat capacity constant pressure (Cp) | 138.9 J/mole•°C) (25°C) (JANAF 1971) | | | | |
| Coefficient of thermal expansion | $0.558 \times 10^{-3}$/°C (20°C) (Perry 1973) | | | | |

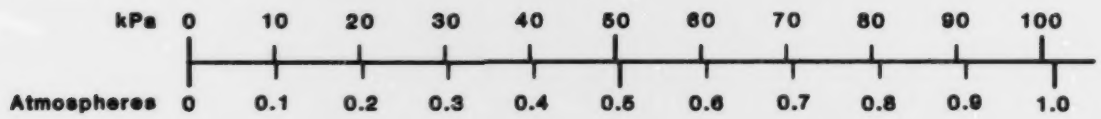
| | Sulphuric Acid | | Oleum | | |
|---|---|---|---|---|---|
| | 95.5-96.5% | 66°Bé | 30% | 25% | 20% |
| Thermal conductivity | | 3.54 mJ/s•cm•°C (32°C) (Lange's Handbook 1979) | 5.2 mJ/s•cm•°C (32°C) (Lange's Handbook 1979) | | |
| Diffusivity | 1.97 x $10^{-5}$ $cm^2/s$ (in water 25°C) (Perry 1973) | | | | |
| pH of aqueous solution | 0.3 (1 N solution 25°C) (CRC 1980) | | | | |
| Eutectic compositions | 36% aqueous solution (freezing point of -64°C) (CIL) | | | | |
| **Solubility** | | | | | |
| In water | Reacts, evolving heat, and mixes slowly with water (CCPA 1982) | | | | |

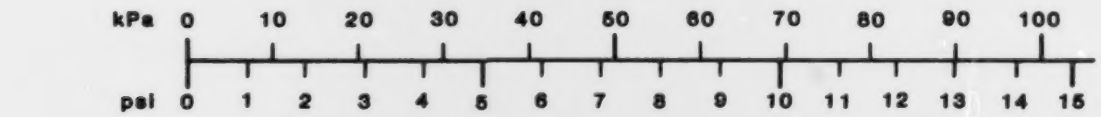
SULPHURIC ACID

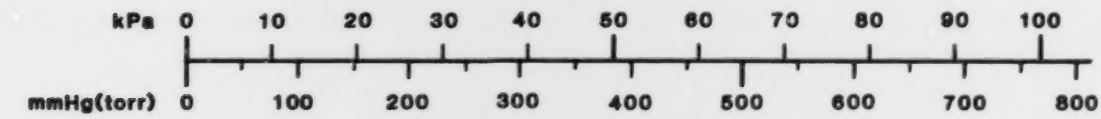
# CONVERSION NOMOGRAMS




**Pressure** 1 kPa = 1,000 Pa




**Viscosity**

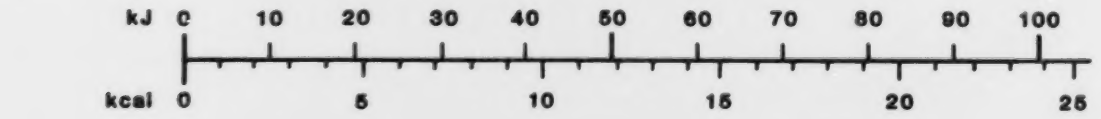
**Dynamic** 1 Pa-s = 1,000 centipoise (cP)

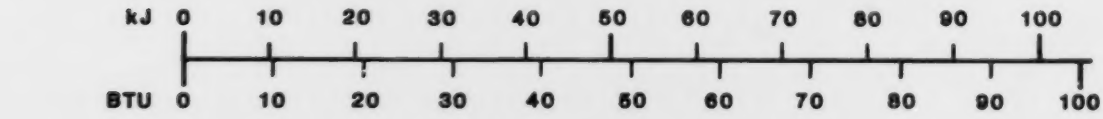
**Kinematic** 1 $m^2/s$ = 1,000,000 centistokes (cSt)

**Concentration (in water)**

1 ppm ≅ 1 mg/L

**Energy (heat)** 1 kJ = 1,000 J



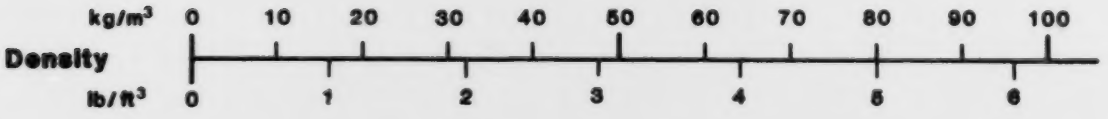



FIGURE 1

SULPHURIC ACID 66° Bé

## LIQUID DENSITY vs TEMPERATURE

Reference: CHRIS 1978

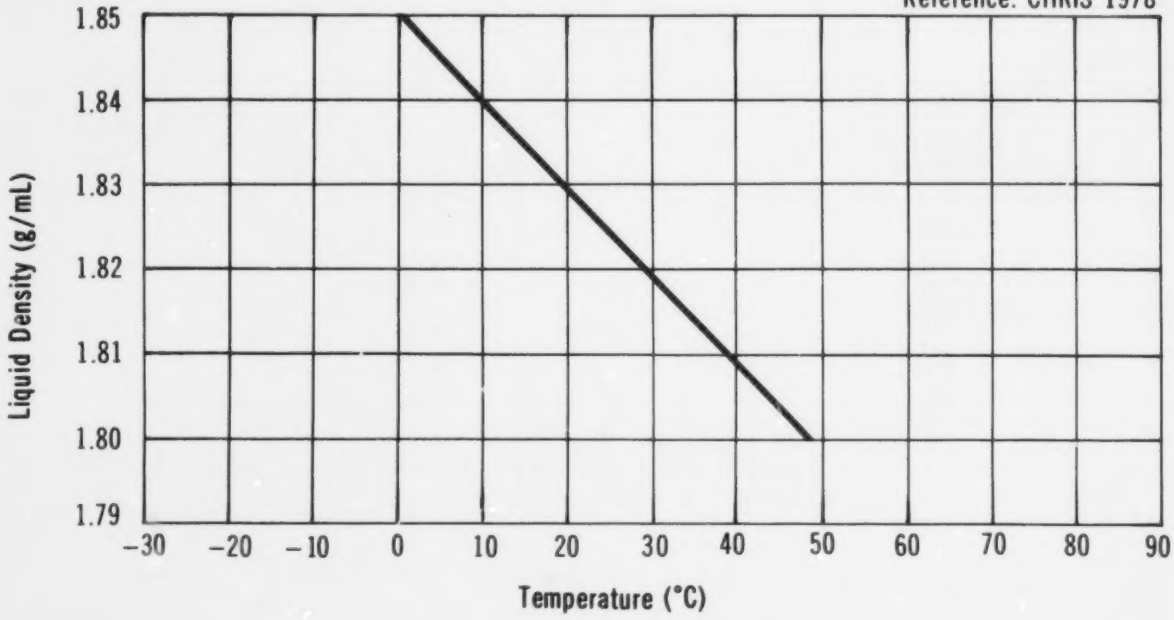



FIGURE 2

SULPHURIC ACID 66° Bé

## LIQUID VISCOSITY vs TEMPERATURE

Reference: CIL

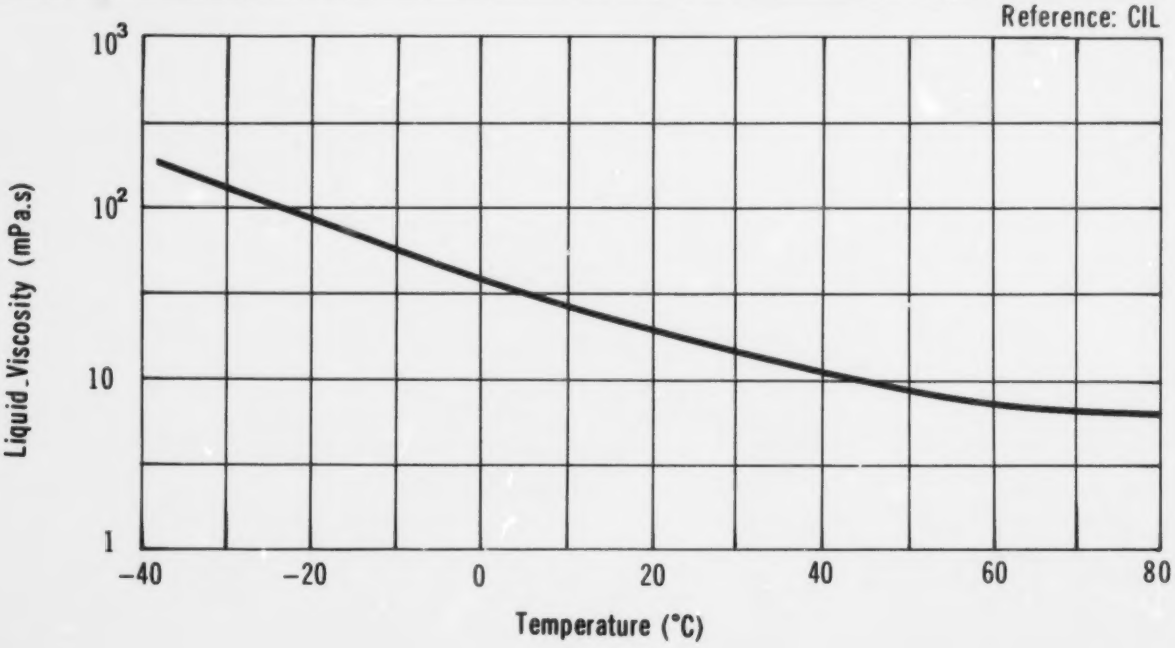
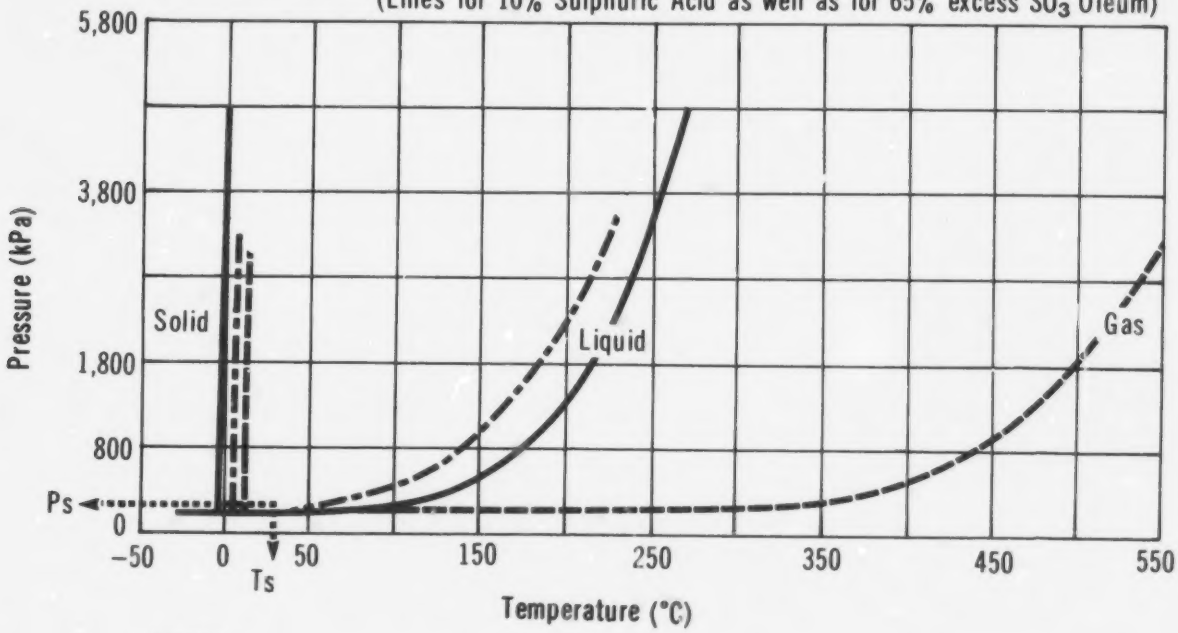


FIGURE 3

SULPHURIC ACID

## PHASE DIAGRAM

(Lines for 10% Sulphuric Acid as well as for 65% excess $SO_3$ Oleum)




LEGEND:

10% acid

Oleum

100% acid

# 3 COMMERCE AND PRODUCTION

## 3.1 Grades, Purities (Corpus 1981; CIL)

**3.1.1 Sulphuric Acid.** Sulphuric acid is sold in Canada in the following grades:

| Grade | Concentration |
|---|---|
| Commercial (66°Bé) | 93.19 percent (min.) |
| Electrolytic (1.835) | 93.19 percent (min.) |
| Chemically Pure | 95.5 to 96.5 percent |

**3.1.2 Oleum.** Oleum, or fuming sulphuric acid, is most often shipped in concentrations of 10 and 20 percent excess $SO_3$ (CCPA 1982).

## 3.2 Domestic Manufacturers

These are corporate headquarters addresses and are not intended as spill response contacts.

**3.2.1 Sulphuric Acid** (Corpus 1981; CCR 1978; Scott 1979).

Allied Chemical Canada Ltd.
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 276-9211

Border Chemical
155 Carlton
Winnipeg, Manitoba
R3C 3H8
(204) 942-8758

Brunswick Mining and Smelting Corp.
Commerce Court West, Suite 4500
P.O. Box 45
Toronto, Ontario
M5L 1B6
(416) 867-7111

Canadian Electrolytic Zinc
860 boul. Cadieux
Valleyfield, Quebec
J6S 4W2
(514) 373-9144

Canadian Industries Limited
45 Sheppard Avenue East
Willowdale, Ontario
M2N 2Z9
(416) 226-6110

Gulf Canada Ltd.
800 Bay Street
Toronto, Ontario
M5S 1Y8
(416) 924-4141

NL Chem Canada Inc.
2140 Sun Life Building
Montreal, Quebec
H3B 2X8
(514) 866-2401, 866-6881

Cominco Ltd.
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 682-0611

DuPont Canada Inc.
Box 2200, Streetsville
Mississauga, Ontario
L5M 2H3

Esso Chemical Canada
2300 Yonge Street
Toronto, Ontario
M5W 1K3
(416) 488-6600

Falconbridge Nickel Mines Ltd.
Commerce Court West
P.O. Box 40
Toronto, Ontario
M5L 1B4

Gaspé Copper Mines
P.O. Box 45
Toronto, Ontario
M5L 1B6
(416) 867-7111

Inco Metals
Inco Ltd.
1 First Canadian Place
P.O. Box 44
Toronto, Ontario
M5X 1C4
(416) 361-7511

Inland Chemicals
Industrial Park
P.O. Box 3180
Fort Saskatchewan, Alberta
T8L 2T2
(403) 998-2225

International Minerals & Chemical
Corp. Canada
701 Evans Avenue, Suite 312
Etobicoke, Ontario
M9C 1A3
(416) 621-9831

Sherritt Gordon Mines Ltd.
P.O. Box 28
Commerce Court West
Toronto, Ontario
M5L 1B1
(416) 363-9241

Sulco Chemicals
60 First Street
Elmira, Ontario
N3B 2Z5
(519) 669-5166

Texasgulf Canada
Commerce Court West
Suite 5000
P.O. Box 175
Toronto, Ontario
M5L 1E7
(416) 869-1200

Western Co-operative Fertilizers Ltd.
111 - 11 Barlow Trail S.E.
P.O. Box 2500
Calgary, Alberta
T2P 2N1
(403) 279-4421

### 3.2.2 **Sulphuric Acid, Fuming (Oleum)** (CCR 1978).

Allied Chemical Canada Ltd.
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 276-9211

Inco Metals (formerly CIL at Copper
Cliff, Ont.)
Inco Ltd.
1 First Canadian Place
P.O. BOX 44
Toronto, Ontario
M5X 1C4
(416) 361-7511

Sulco Chemicals Ltd.
60 First Street
Elmira, Ontario
N3B 2Z5
(519) 669-5166

### 3.3 Other Suppliers (Corpus 1981)

Noranda Sales Corp. Ltd.
Commerce Court West
P.O. Box 45
Toronto, Ontario
M5L 1B6
(416) 867-7111

### 3.4 Major Transportation Routes

Current Canadian production of sulphuric acid is very widespread, occurring in seven provinces. 49.2 percent of sulphuric acid is primarily for captive use. The largest production facilities (non-captive) are located near Montreal and the Gaspé Peninsula, Quebec; Sudbury and Timmins, Ontario; near Winnipeg, Manitoba; in Fort Saskatchewan (near Edmonton), Alberta; and in Trail, B.C. (southeast B.C.). Transportation is mainly by rail and tank truck.

### 3.5 Production Levels (Corpus 1980; CCPA 1982)

| Company, Plant Location | Nameplate Capacity kilotonnes/yr (1980) |
|---|---|
| Allied Chemical Canada, Valleyfield, Que. | 113 |
| Border Chemical, Transcona, Man. | 150 |
| Brunswick Mining and Smelting, Belledune, N.B.* | 180 |
| Canadian Electrolytic Zinc, Valleyfield, Que. | 120 |
| CIL, McMaster, Que. | 60 |
| NL Chem Canada, Varennes, Que.* | 47 |
| Cominco, Trail, B.C. | 440 |
| Cominco, Kimberly, B.C.* | 280 |
| Esso Chemical Canada, Redwater, Alta.* | 515 |
| Falconbridge Nickel, Sudbury, Ont.* | 320 |
| Gaspé Copper Mines, Murdochville, Que. | 245 |
| Gulf Minerals, Rabbit Lake, Sask.* | 45 |
| Inland Chemicals, Ft. Saskatchewan, Alta. | 125 |
| Inland Chemicals, Prince George, B.C. | 35 |
| INCO, Copper Cliff, Ont. | 900 |
| International Minerals and Chemicals, Pt. Maitland, Ont.* | 250 |
| Sherritt Gordon Mines, Ft. Saskatchewan, Alta. | 190 |

| Company, Plant Location | Nameplate Capacity kilotonnes/yr (1980) |
|---|---|
| Sulco Chemicals, Elmira, Ont. | 35 |
| Texasgulf Canada, Timmins, Ont. | 205 |
| Western Co-operative Fertilizers, Calgary, Alta.* | 360 |
| Western Co-operative Fertilizers, Medicine Hat, Alta.* | 190 |
| TOTAL | 4,805 |
| Domestic Production (1980) | 4,296.5 |
| Imports (1980) | 18 |
| TOTAL | 4,314.5 |

*Primarily for captive use.

### 3.6 Future Development

Two plants under construction, Texasgulf in Timmins, Ontario, and Western Co-operative Fertilizers in Medicine Hat, Alberta, will have increased sulphuric acid capacity: 200 kt/yr for Texasgulf and 397 kt/yr for Western Co-operative Fertilizers (existing unit to be replaced) (CCP 1981).

Cominco Ltd. has started to upgrade its acidification plant at Trail, B.C., resulting in a capacity of 380 kt/yr (Eco/Log 1981).

### 3.7 The Manufacture of Sulphuric Acid and Oleum (Shreve 1977; CCPA 1982)

**3.7.1 General.** The manufacture of sulphuric acid in Canada is primarily from smelter flue gas ($SO_2$) recovery.

**3.7.2 Manufacturing Process.** The process reactions are as follows:

$$S + O_2 \longrightarrow SO_2 \text{ (all gaseous)}$$
$$SO_2 + 1/2\ O_2 \longrightarrow SO_3 \text{ (all gaseous)}$$
$$SO_3 + H_2O \longrightarrow H_2SO_4 \text{ (liquid)}$$

The raw (elemental) sulphur is melted, atomized, and burned in air, resulting in the production of sulphur dioxide. Alternatively, $SO_2$ is obtained from smelter flue gas recovery. The sulphur dioxide is passed through a converter which contains a catalyst. Sulphur trioxide is emitted from the converter and is then put through an absorbing tower with water and low strength sulphuric acid to form commercial grades.

To produce oleum, concentrated sulphuric acid is mixed with sulphur trioxide. The resulting product is anhydrous sulphuric acid with a certain percentage of free sulphur trioxide.

**3.8 Major Uses in Canada** (Corpus 1981; CCP 1981)

Sulphuric acid is a widely used chemical in the world and has may applications. Some uses include the production of phosphoric acid, hydrofluoric acid, phosphatic fertilizers, aluminum sulphate, ammonium sulphate, superphosphates, cellulose film, viscose rayon, soaps and detergents, organic chemicals, explosives, and titanium dioxide. It is also used in the following industries: uranium ore processing, mining and smelting, pulp and paper, and petroleum refining.

**3.9 Major Buyers in Canada** (Corpus 1981; CBG 1980)

Abitibi-Price, Smooth Rock Falls, Ont; Jonquiere, Que.
Agnew Lake Mines, Agnew Lake, Ont.
Alcan Smelters & Chemicals, Jonquiere, Que.
Algoma Steel, Sault Ste. Marie, Ont.
Allied Chemical Canada, Amherstburg, Ont.
American Can, Marathon, Ont.
BP Canada, Oakville, Ont.
Bate Chemical, Toronto, Ont.
Bayer (Canada), Mississauga, Ont.
Benson Chemicals, Freelton, Ont.
Boise-Cascade, Ft. Frances, Newcastle, N.B.
British Columbia Forest Products, Crofton, B.C.
Canada Colours & Chem., Toronto, Ont.
Canada Wire & Cable, Belledune, N.B.
Canadian Cellulose, Prince Rupert, B.C.
Canadian Copper Refiners, Montreal, Que.
Canadian Forest Products, Pt. Mellon, B.C.
Canadian International Paper, La Tuque, Que.
Cariboo Pulp & Paper, Quesnel, B.C.
Colgate-Palmolive, Toronto, Ont.
Consolidated-Bathurst, Pontiac Mill, Que.
Courtaulds Canada, Cornwall, Ont.
Crestbrook Forest, Skookumchuck, B.C.
Crown Zellerbach, Campbell River, B.C.
Denison Mines, Elliot Lake, Ont.
Dominion Foundries, Hamilton, Ont.
Domtar, Lac Quevillon, Que.; Cornwall, Ont.
Donohue St-Felicien, St-Felicien, Que.
DuPont Canada, Shawinigan, Que.; North Bay, Ont.
Eddy Forest Products, Espanola, Ont.
Eurocan Pulp, Kitimat, B.C.
Great Lakes Forest, Thunder Bay, Dryden, Ont.
Gulf Canada, Montreal East, Que.
Gulf Canada, Port Moody, B.C.

Kert Chemical, Toronto, Ont.
Kimberly-Clark of Canada, Terrace Bay, Ont.
Inco, Copper Cliff, Ont.
Intercontinental Paper, Prince George, B.C.
Irving Pulp & Paper, Saint John, N.B.
Lever Detergents, Toronto, Ont.
M & T Chemicals Ltd., Hamilton, Ont.
MacMillan Bloedel, Nanaimo, Pt. Alberni, B.C.
Madawaska Mines, Bancroft, Ont.
NL Chem Canada, Varennes, Que.
Northwood Pulp, Prince George, B.C.
Ontario Paper, Thorold, Ont.
Petrofina, Pte-aux-Trembles, Que.
Price, Kenogami, Que.
Prince Albert Pulp, Prince Albert, Sask.
Prince George Pulp & Paper, Prince George, B.C.
Procter & Gamble, Hamilton, Ont.
Procter & Gamble Cellulose, Grande Prairie, Alta.
Rayonier Canada, Woodfibre, B.C.
Rio Algom, Elliot Lake, Ont.
Ste Anne-Nackawic, Nackawic, N.B.
St. Regis, Hinton, Alta.
Scott Maritimes, Pt. Abercrombie, N.S.
Shefford Chemicals, Granby, Que.
Shell Canada, Oakville, Ont.; Montreal, Que.
Steel Co. of Canada, Hamilton, Ont.
Tahsis, Gold River, B.C.
Texaco Canada, Montreal East, Que.; Nanticoke, Ont.
Thurso Pulp & Paper, Thurso, Que.
Tioxide of Canada, Tracy, Que.
Uba Chemical, Mississauga, Ont.
VanWaters & Rogers, Richmond, B.C.
Weyerhaeuser Canada, Kamloops, B.C.

# 4 MATERIAL HANDLING AND COMPATIBILITY

## 4.1 Containers and Transportation Vessels

**4.1.1 Bulk Shipment.** Sulphuric acid solutions, oleum, and spent acid are shipped bulk in specially designed railway tank cars and tank motor vehicles.

**4.1.1.1 Railway tank cars.** Railway tank cars used in the transportation of sulphuric acid are classified under the A-1 Class 103, A-3 Class 105A and A-8 Class III CTC tanker specifications. See Table 2 for a description under each specification. Most cars for sulphuric acid service are lined with Heresite resin.

The acid is usually shipped in CTC 103AW and 111A100W2 railway cars, as shown in Figures 4 and 5. Tables 3 and 4 indicate railway tank car details associated with these drawings. Sulphuric acid cars are unloaded through bottom outlets under special CTC permits only. Typically, cars are unloaded from the top using compressed air (MCA 1963). The sulphuric acid is withdrawn through an eduction pipe which extends from the bottom of the tank to the top operating platform where it terminates with a 51 mm (2 in.) unloading connection valve. Air pressure of 207 kPa (30 psi) is applied through the 25 mm (1 in.) air connection valve.

Outside heating coils and fibreglass insulation are required for certain strengths of acid that freeze at common winter temperatures. Occasionally for munition manufacture, nitric acid may be added as an antifreeze agent to sulphuric acid, particularly to oleum (MCA 1963; CCPA 1982).

A safety relief valve set at 518 kPa (75 psi) or a safety vent set at 690 kPa (100 psi) is required on top of the rail car. Rupture disc settings of not more than 100% of tank test pressure on 103AW, 111A100W2 and 111A100W5 are also authorized by the CTC under special permits. A gauging device, either the rod type or the tape type, is optional. The maximum pressure allowable for the CTC 111A100W2 rail cars is 448 kPa (65 psi). When the 111A60W2 cars are used, this maximum pressure would be 276 kPa (40 psi) (TCM 1979). Both these pressures exceed the maximum compressed air pressure of 207 kPa (30 psi) used during unloading. Sulphuric acid is never transported under pressure.

Sulphuric acid cars are filled through a 200 mm (8 in.) opening at the top of the car. As indicated in Figures 4 and 5, a domeless manway or dome option is available depending on the class of car (TCM 1979). When a bottom washout is used, depending again on the class of car selected, a washout plug and "O" ring assembly is

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS

| DOT* and CTC** Specification Number | | |
|---|---|---|
| Sol'n >65% inc. Oleum | Sol'n <51% | Description |
| 103W | | Steel fusion-welded tank with dome.<br>Uninsulated or insulated.<br>Bottom outlet or washout optional. |
| 103AW | | Steel fusion-welded tank with dome.<br>Uninsulated or insulated.<br>Top unloading arrangement required.<br>Bottom outlet prohibited; bottom washout optional. |
| | 103BW | Steel fusion-welded tank with dome.<br>Uninsulated or insulated.<br>PVC-lined tank.<br>Top unloading arrangement required.<br>Bottom outlet or washout prohibited. |
| 103CW | | Alloy (stainless) steel fusion-welded tank with dome.<br>Insulated or uninsulated. 1% dome.<br>Bottom outlet or washout prohibited.<br>Top unloading arrangement required. |
| 111A60W2 (use also for sol'ns >51% and <65% with rubber lining) | | Steel fusion-welded tank without dome.<br>Uninsulated or insulated.<br>2% minimum outage.<br>Gauging device.<br>Top unloading arrangement required.<br>Bottom outlet prohibited; bottom washout optional.<br>Test pressure 414 kPa (60 psi). |
| 111A100W2 (use also for sol'ns >51% and <65% with rubber lining) | | Steel fusion-welded tank without dome.<br>Uninsulated or insulated.<br>2% minimum outage.<br>Gauging device.<br>Top unloading arrangement required.<br>Bottom outlet prohibited; bottom washout optional.<br>Test pressure 690 kPa (100 psi). |

TABLE 2 RAILWAY TANK CAR SPECIFICATIONS (cont'd)

| DOT* and CTC** Specification Number | | |
|---|---|---|
| Sol'n >65% inc. Oleum | Sol'n <51% | Description |
| | 111A60W5 | Steel fusion-welded tank without dome.<br>Uninsulated or insulated.<br>PVC-lined tank.<br>2% minimum outage.<br>Gauging device.<br>Top unloading arrangement required.<br>Bottom outlet or washout prohibited.<br>Test pressure 414 kPa (60 psi). |
| 111A100W6 | | Alloy (stainless) steel fusion-welded tank without dome.<br>Insulated or uninsulated.<br>Gauging device.<br>Top unloading arrangement required.<br>Bottom outlet or washout prohibited.<br>Test pressure 690 kPa (100 psi). |
| 111A100F2 | | Steel forge-welded tank without dome.<br>Uninsulated or insulated.<br>2% minimum outage.<br>Gauging device.<br>Top unloading arrangement required.<br>Bottom outlet prohibited; bottom washout optional.<br>Test pressure 690 kPa (100 psi). |

* Department of Transportation (U.S.)
** Canadian Transport Commission

required in conjunction with a separate nozzle flange and blind flange gasket. A tell-tale plug between both assemblies is required (TCM 1979).

**4.1.1.2 Tank motor vehicles.** The capacities of tank trucks transporting sulphuric acid range from 15 to 28 tonnes, with 22 tonnes being most common.

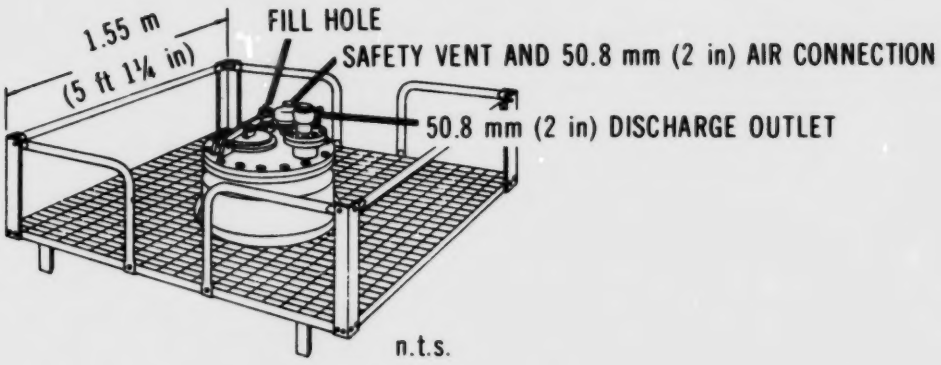
Similar to railway tank cars, these highway tankers are unloaded from the top. Compressed air is used for unloading. The air inlet is usually a 25 mm (1 in.) diameter male threaded connection located at the top of the trailer through which air pressure not

FIGURE 4

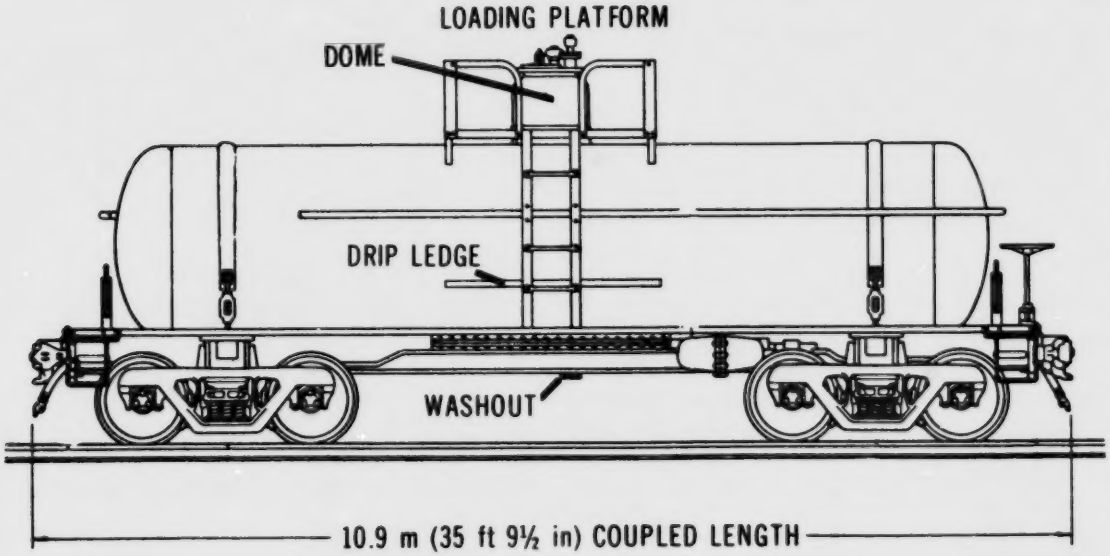
SULPHURIC ACID

**RAILWAY TANK CAR - CLASS 103 AW**

(Reference - TCM 1979; AAR 1982; RTDCR 1974)




**Detail of loading platform**




Approximate Scale 1 : 7

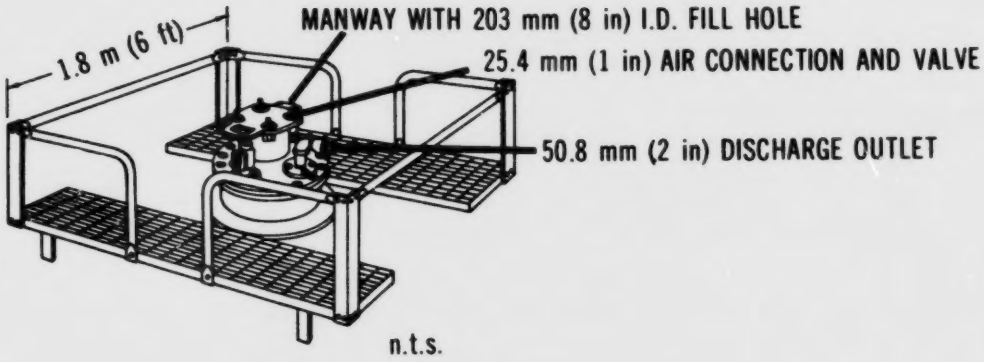
**Illustration of train car layout**

FIGURE 5

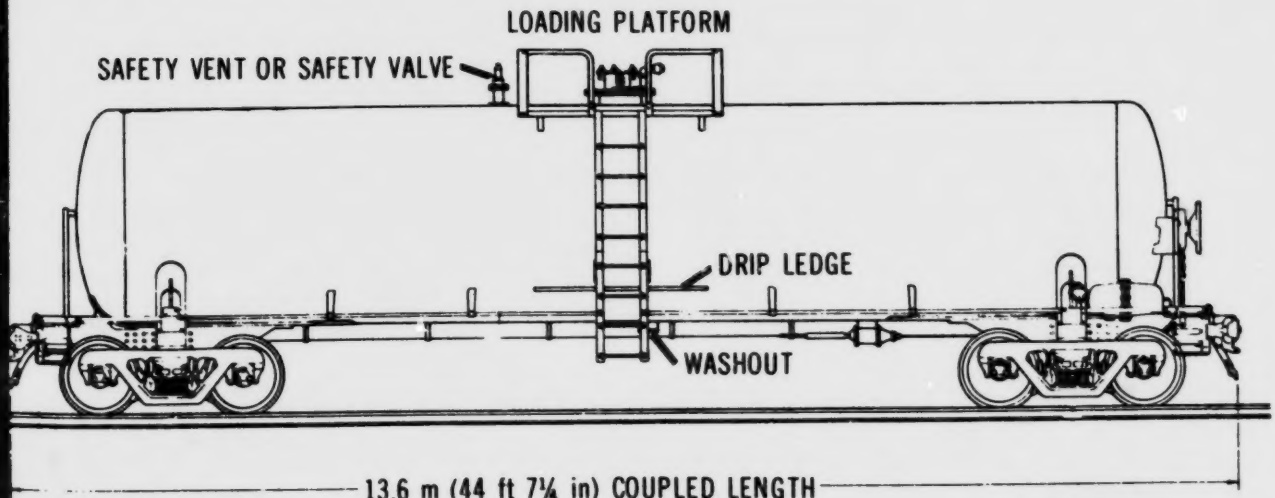
SULPHURIC ACID

**RAILWAY TANK CAR - CLASS 111A100W2**

(Reference - TCM 1979, AAR 1982, RTDCR 1974)




**Detail of loading platform**




Approximate Scale 1 : 72

**Illustration of train car layout**

TABLE 3 RAILWAY TANK CAR DETAILS - CLASS 103AW (TCM 1979; AAR 1982; RTDCR 1974)

| | Description | Dimension | Notes |
|---|---|---|---|
| Overall | Nominal capacity | 26,500 L (5,800 gal.) | |
| | Car weight-empty | 19,200 kg (42,400 lb.) | |
| | Car weight-full | 80,300 kg (117,000 lb.) | |
| Tank | Material | | Steel |
| | Thickness | 14.3 mm (9/16 in.) | |
| | Inside diameter | 1.95 m (77 in.) | |
| | Test pressure | 414 kPa (60 psi) | |
| | Burst pressure | 1,650 kPa (240 psi) | |
| Typical Dimensions | Coupled length | 10.9 m (35 ft 9 1/2 in.) | |
| | Length over strikers | 10.1 m (33 ft 2 in.) | |
| | Length of truck centers | 6.77 m (22 ft 2 1/2 in.) | |
| | Height to top of grating | 3.08 m (10 ft 1 1/4 in.) | |
| | Overall height | 4.20 m (13 ft 9 3/8 in.) | |
| | Overall width (over grabs) | 3.10 m (10 ft 2 in.) | |
| | Coupler height over rail | 0.88 m (2 ft 10 1/2 in.) | |
| | Length of grating | 2.25 m (7 ft 4 5/8 in.) | |
| | Width of grating | 1.86 m (6 ft 1 1/8 in.) | |
| Loading/ Unloading Fixtures | Unloading connection | 51 mm (2 in.) | |
| | Fill hole | 152-203 mm (6-8 in.) | quick-opening type |
| | Air connection | 51 mm (2 in.) | |
| | Bottom outlet | | prohibited, CTC approval |
| | Bottom washout | 152-203 mm (6-8 in.) | required for bottom unloading |
| Safety Devices | Safety vent | | required, may be equipped with frangible disc with 3 mm (1/8 in.) vent hole except for oleum service |
| Dome | | | required, provides 1% expansion capacity |
| Insulation | | | Optional |

TABLE 4 RAILWAY TANK CAR DETAILS - CLASS 111A100W2 (TCM 1979; AAR 1982; RTDCR 1974)

| | Description | Dimension | Notes |
|---|---|---|---|
| Overall | Nominal capacity | 50,500 L (11,100 gal.) | |
| | Car weight-empty | 25,200 kg (55,600 lb.) | |
| | Car weight-full | 119,300 kg (263,000 lb.) | |
| Tank | Material | | Aluminum Alloy |
| | Thickness | 14.3 mm (9/16 in.) | |
| | Inside diameter | 2.40 m (94 1/2 in.) | |
| | Test pressure | 690 kPa (100 psi) | |
| | Burst pressure | 3,450 kPa (500 psi) | |
| Typical Dimensions | Coupled length | 13.6 m (44 ft 7 1/4 in.) | |
| | Length over strikers | 12.8 m (41 ft 11 3/4 in.) | |
| | Length of truck centers | 9.46 m (31 ft 0 1/4 in.) | |
| | Height to top of grating | 3.48 m (11 ft 5 13/16 in.) | |
| | Overall height | 4.26 m (13 ft 11 13/16 in.) | |
| | Overall width (over grabs) | 3.21 m (10 ft 6 1/2 in.) | |
| | Coupler height over rail | 0.88 m (2 ft 10 1/2 in.) | |
| | Length of grating | 2.44 m (8 ft 0 1/8 in.) | |
| | Width of grating | 1.83 m (6 ft) | |
| Loading/ Unloading Fixtures | Unloading connection | 51 mm (2 in.) | |
| | Fill hole | 203 mm (8 in.) | |
| | Air connection | 25 mm (1 in.) | |
| | Bottom outlet | | prohibited, CTC approval |
| | Bottom washout | 152-203 mm (6-8 in.) | required for bottom unloading |
| Safety Devices | Safety vent | | required, may be equipped with frangible disc with 3 mm (1/8 in.) vent hole except for oleum service |
| Insulation | | | Optional |
| Dome | | | None |

exceeding 207 kPa (30 psi) may be applied. Tanks may be insulated and heated depending on the acid strength and freezing point (CSA 1976).

Tank motor vehicles must conform to Transport Canada specification TC312, covering MC310, MC311, MC312 as outlined in Table 5 (TDGC 1980). Sulphuric acid solutions are not transported under pressure. Highway tankers must be pressure tested at 311 kPa (45 psi) minimum to allow for the compressed air pressure of 207 kPa (30 psi) used during top unloading (CSA 1976). The maximum working pressure of the tanker is in effect 207 kPa (30 psi).

TABLE 5 TANK MOTOR VEHICLE SPECIFICATIONS

| TC* Specification Number | Description |
|---|---|
| TC312 | Steel butt-welded tank. |
| | Design and construct in accordance with ASME code when unloading by pressure in excess of 103 kPa (15 psi). |
| | Gauging device not required. |
| | Top and/or bottom discharge outlet. |
| | Bottom discharge outlet must have remotely operated handles. |
| | Minimum one pressure relief device per compartment as required by ASME code. |
| | One minimum 380 mm (15 in.) diameter manhole per compartment. |
| | Bottom washout optional. |

* Transport Canada

**4.1.2 Packaging.** In addition to bulk shipments, sulphuric acid is also transported in drums, although again this practice is infrequent in Canada. Drums fabricated from a variety of construction materials are permitted. Tables 6 and 7 listing drum types and descriptions for oleum and for sulphuric and spent acid are included (TDGC 1980).

Glass carboys, boxed or in expanded polyethylene containers, are also used to transport oleum and sulphuric acid (MCA 1963).

## 4.2 Off-loading

**4.2.1 Off-loading Equipment and Procedures for Railway Tank Cars.** The following procedures are derived from literature sources and are included to provide information which may be of use in spill events. Readers are advised to consult with experts from industry in the event that this information is required.

Prior to off-loading, certain precautions must be taken (MCA 1963):

- The vented storage tank must be checked to make sure that it will hold the contents of the car.
- For night-time unloading, lights must have an explosion-proof rating.
- Personnel must not enter the car under any circumstances.
- Brakes must be set, wheels chocked, derails placed and caution placards displayed.
- A safe operating platform must be provided at the unloading point.

Proceed with off-loading as follows (MCA 1963):

- In cold weather for certain strengths of acid, connect steam coil connection valves to live steam.
- Connect the 51 mm (2 in.) unloading line to the discharge outlet and connect the 25 mm (1 in.) air line. Air pressure must be reduced to 207 kPa (30 psi) for unloading. A safety relief valve must be installed in the air line to release at 242 kPa (35 psi).
- After opening the air supply valve, the unloading connection valve can then be opened to unload the car.
- Once the car is empty, the air supply valve must be closed and the vent valve in the air line opened to allow the line pressure to equalize to atmospheric pressure.
- Reverse the above procedure to close up the car.

**4.2.2 Off-loading Equipment and Procedures for Tank Motor Vehicles.** The unloading of sulphuric acid tank trailers is similar to that of railway tank cars. The general procedures for tank cars apply equally well to tank trailers.

TABLE 6 DRUMS FOR OLEUM

| Type of Drum | Designation | Description | Figure No. (if any) |
|---|---|---|---|
| Steel | 1A1 | Nonremovable head, reusable | 6 |
| | 1A1A | 1A1 with reinforced chime | 6 |
| | 1A1B | 1A1 with welded closure flange | 6 |
| | 1A1C | 1A1 with lead coating | 6 |
| | 1A1D | 1A1 with coating (other than lead) | 6 |
| | 1A2 | Removable head, reusable | 6 |
| Monel* | TC5M | | 6 |
| Nickel | TC5K | Similar to monel drum, only nickel | 6 |

*See Section 4.3 of this report.

TABLE 7 DRUMS FOR SULPHURIC ACID AND SPENT ACID

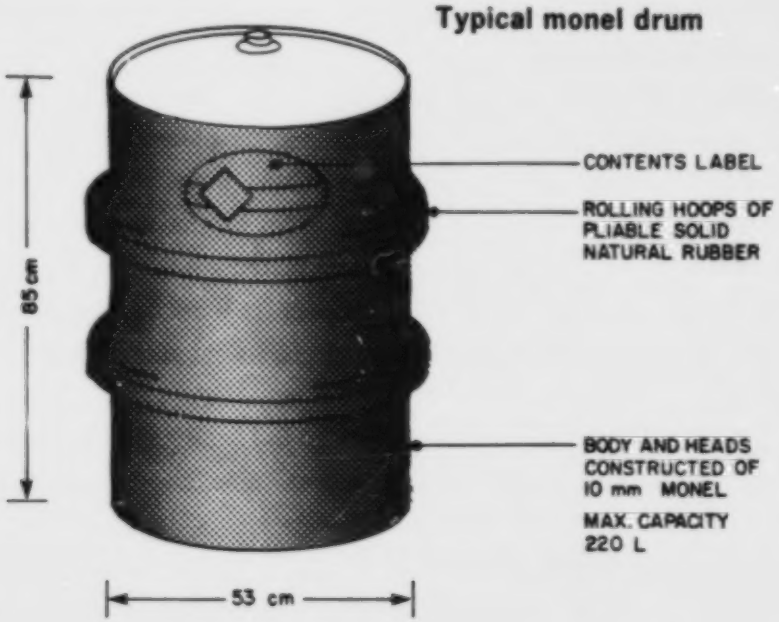
| Type of Drum | Designation | Description | Figure No. (if any) |
|---|---|---|---|
| Steel | 1A1 | Nonremovable head, reusable | 6 |
| | 1A1A | 1A1 with reinforced chime | 6 |
| | 1A1B | 1A1 with welded closure flange | 6 |
| | 1A1C | 1A1 with lead coating | 6 |
| | 1A1D | 1A1 with coating (other than lead) | 6 |
| | 1A3 | Nonremovable head, single use only | 6 |
| Plastic | 1H1 | Nonremovable head. Maximum capacity 250 L. Maximum net mass 400 kg | |
| Steel Drums with inner plastic receptacles | 6HA1 | Outer steel sheet in the shape of drum. Inner plastic receptacle. Maximum capacity 225 L | |

FIGURE 6

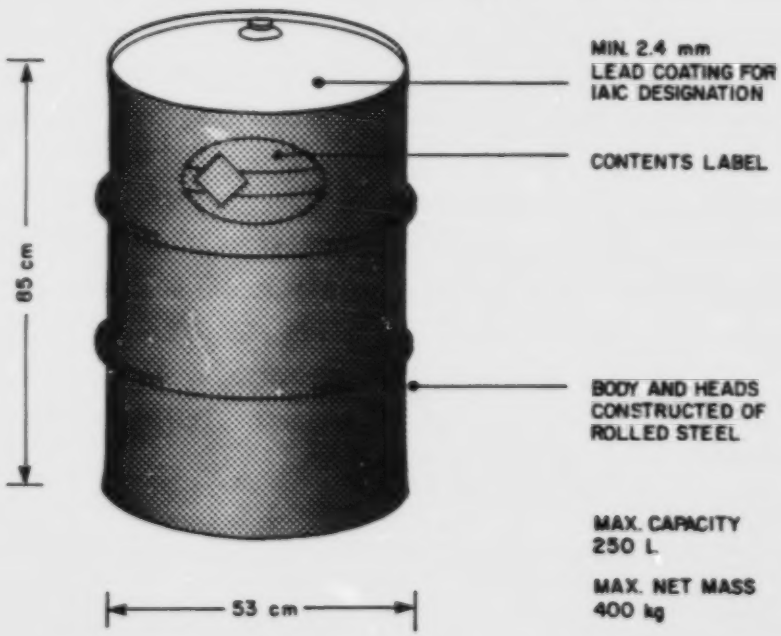
SULPHURIC ACID

## TYPICAL DRUM CONTAINERS

**Typical monel drum**


CONTENTS LABEL
ROLLING HOOPS OF PLIABLE SOLID NATURAL RUBBER
BODY AND HEADS CONSTRUCTED OF 10 mm MONEL
MAX. CAPACITY 220 L
85 cm
53 cm

**Typical steel drum**


MIN. 2.4 mm LEAD COATING FOR IAIC DESIGNATION
CONTENTS LABEL
BODY AND HEADS CONSTRUCTED OF ROLLED STEEL
MAX. CAPACITY 250 L
MAX. NET MASS 400 kg
85 cm
53 cm

**4.2.3 Specifications and Materials for Off-loading Equipment.** The materials of construction for off-loading system components discussed in this section along with specifications refer to those generally used in sulphuric acid service. The components of a typical off-loading system include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Schedule 80 seamless ASTM A106 carbon steel or Schedule 40 stainless steel 316 pipes and welding fittings are recommended for oleum and commercial sulphuric acid (MCA 1963). Flanged joints should be used and these should be welded, because threaded pipes and fittings tend to leak. Stress relief at the weld will also lengthen the serviceability of the pipe. The pipe line should be tested with air at pressures from 345 to 518 kPa (50 to 75 psi) and all leaks carefully stopped. If leaks develop in service, the only satisfactory way to repair them is to chip out the bad weld and reweld, or to replace the section of pipe.

The unloading line should be 51 mm (2 in.) pipe because this is the standard fitting on sulphuric acid tank cars; however, process pipe may be almost any size. Pipe under 25 mm (1 in.), however, is not recommended.

Outdoor lines must be self-draining and may be insulated depending upon acid strength. These can be steam traced with 9 mm to 13 mm (3/8 to 1/2 in.) copper tubing or steel pipe located inside the insulation (CSA 1976).

Steel or stainless steel pipe and swivel joints may be used for flexible sections when handling oleum. Either the ball bearing type swivel joint or the simple stuffing box type will give adequate service with proper maintenance. Flexible acid hose is normally used to handle oleum and sulphuric acid. Chemiflex 951 gives satisfactory service for all strengths of sulphuric acid up to 98/99 percent. Teflon-lined Chemiflex 976 is suitable for oleum up to 30 percent strength (CSA 1976).

For valving, quick acting ball or plug valves in "20" alloy will serve adequately in all sulphuric acid and oleum applications (ASA 1978).

Teflon gaskets can be used as a gasket material in all sulphuric acid strengths (DCRG 1978).

A single suction centrifugal pump with "20" alloy shaft and impeller and a high silicon cast iron casing is recommended for pumping. Teflon again is a good packing material (CSA 1976).

Welded heavy wall carbon steel or stainless steel storage tanks are commonly used. Fibre-reinforced plastic or PVC lined steel is commonly used for solutions up to 70 percent sulphuric acid (CSA 1976).

### 4.3 Compatibility with Materials of Construction

The compatibility of sulphuric acid with materials of construction is shown in Table 8. The unbracketed abbreviations are described in Table 9.

The rating system used in Table 8 is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| 1. Pipes and Fittings | 54-60°Bé | | CS, Sch. 80 and 150 lb. Welding Flanges | | |
| | 66°Bé-100% | | CI and 250 lb. Welding Flanges (DSA) | | |
| | Electrolyte and Other Grades up to 60°Bé | | Lead, with 6% Antimony 125 lb. Flanges or Lap Joint Flanges | | |
| | | | High Silicon Cast Iron | | |
| | | | Rigid Normal Impact uPVC, Sch. 80 (DSA) | | |
| | Electrolyte | | Lead, with 6% Antimony Lead 125 lb. | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | 66°Bé | | Flanges or Lap Joint Flanges<br><br>High Silicon Cast Iron (DSA) | | |
| | Chemically Pure 95.5 to 96.5% | | Pyrex Glass<br><br>PTFE Plastic Lined Hose (DSA) | | |
| | Oleum, All Strengths | | CS, Sch. 80 and 150 lb. Welding Flanges (DSA) | | CI, High Silicon Cast Iron (DSA) |
| | 10-75% | 23 | PE<br><br>PVC I<br>PVC II (DPPED 1967) | | ABS (DPPED 1967) |
| | 10-75% | 49 | | | PE (DPPED 1967) |
| | 10-75% | 60 | PVC I | | PVC II (DPPED 1967) |
| | 75-90% | 23 | PVC I | | PE<br>ABS<br>PVC II (DPPED 1967) |
| | 75-90% | 60 | | PVC I (DPPED 1967) | |
| | 16% | 121 | PVDF<br>Chlorinated Polyether (DCRG 1978) | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | 16% | 93 | PP (DCRG 1978) | | |
| | 16% | 52 | PVDC (DCRG 1978) | | |
| | 60% | 121 | Chlorinated Polyether (DCRG 1978) | | |
| | 60% | 121 | PVDF (DCRG 1978) | | PVDC (DCRG 1978) |
| | 60% | 107 | PVDF (DCRG 1978) | | PVDC (DCRG 1978) |
| | 60% | 93 | PP (DCRG 1978) | | PVDC (DCRG 1978) |
| | 93% | 79 | PVDF | | PVDC (DCRG 1978) |
| | | | PP (DCRG 1978) | | |
| | 93% | 66 | Chlorinated Polyether | | PVDC (DCRG 1978) |
| | 98% | 66 | PVDF (DCRG 1978) | | PVDC (DCRG 1978) |
| | 98% | 52 | PP (DCRG 1978) | | PVDC (DCRG 1978) |
| 2. Valves | 54-60°Bé 66°Bé - 100% | | "20" Alloy With PTFE Plastic Packing and 150 lb. Flanges | | |
| | | | Plug-type, "20", PTFE Plastic Sleeve and 150 lb. Flanges (DSA) | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | Electrolyte and Other Grades up to 60°Bé | | "20" Alloy or High Silicon Cast Iron with PTFE Plastic Packing and 150 lb. Flanges | | |
| | | | 6% Antimony Lead with PTFE Plastic Packing and 125 lb. Flanges | | |
| | | | Plug-type, "20" Alloy, PTFE Plastic Sleeve and 150 lb. Flanges (DSA) | | |
| | Electrolyte 66°Bé | | "20" Alloy or High Silicon Iron with PTFE Plastic Packing and 150 lb. Flanges | | |
| | | | 6% Antimony Lead with PTFE Plastic Packing and 125 lb. Flanges | | |
| | | | Plug-type, "20" Alloy, PTFE Plastic Sleeve and 150 lb. Flanges (DSA) | | |
| | Chemically | | Porcelain "Y" Valves | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | Pure 95.5 to 96.5% | | with PTFE Plastic Discs and 150 lb. Flanges (DSA) | | |
| | Oleum All Strengths | | "20" Alloy with PTFE Plastic Packing and 150 lb. Flanges | | |
| | | | Plug-type, "20" Alloy, PTFE Plastic Sleeve and 150 lb. Flanges (DSA) | | |
| | 50% (41°Bé) | 21 | SS 316 (JSSV 1979) | | |
| | 50% (41°Bé) | Boiling | | | SS 316 (JSSV 1979) |
| | Concen-trated (66°Bé) | 21 | SS 316 (JSSV 1979) | | |
| | Concen-trated (66°Bé) | Boiling | | SS 316 (JSSV 1979) | |
| 3. Pumps | >77% | Cold | All Iron High Silicon Cast Iron (HIS 1969) | | |
| | 65-93% | >79 | High Silicon Cast Iron (HIS 1969) | | |
| | 65-93% | <79 | High Silicon Cast Iron (HIS 1969) | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | 10-65% | | High Silicon Cast Iron (HIS 1969) | | |
| | 54°-60°Bé | | Centrifugal Type "20" Alloy | | |
| | 60°Bé - 100% | | CI with "20" Alloy Impeller | | |
| | | | High Silicon Cast Iron (DSA) | | |
| | Electro-lyte and Other Grades up to 60°Bé | | Centrifugal type | | |
| | | | "20" Alloy | | |
| | | | High Silicon Cast Iron (DSA) | | |
| | Electro-lyte 66°Bé | | Centrifugal type | | |
| | | | "20" Alloy | | |
| | | | High Silicon Cast Iron (DSA) | | |
| | Chemically Pure 95.5 to 96.5% | | Centrifugal type, Glass Lined | | |
| | | | Diaphragm type with PTFE Plastic Diaphragm (DSA) | | |
| | Oleum - All Strengths | | Centrifugal type, "20" Alloy (DSA) | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| 4. Storage | 54° - 60°Bé | | Heavy Steel (DSA) | | |
| | 93 to 100% | | | | |
| | Electro-lyte and Other Grades up to 60°Bé | | Steel or Wood with Chemical Lead Lining (DSA) | | |
| | Electro-lyte 66°Bé | | Steel or Wood with Chemical Lead Lining | | |
| | | | Steel with Baked Phenolic Lining (i.e. Heresite P-403) (DSA) | | |
| | Chemi-cally Pure 95.5 to 96.5% | | Glass Lined Steel (DSA) | | |
| | Oleum All Strengths | | Heavy Steel (DSA) | | |
| 5. Others | 10% | 60 | PVC (TPS 1978) | | |
| | 10% | 100 | CPVC (TPS 1978) | | |
| | 10% | 82 | PP (TPS 1978) | | |
| | 10% | | NR<br>SBR<br>CR<br>NBR<br>IIR | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | | | CSM<br>Si<br>EPDM (GPP) | | |
| | 15% | 20 | SS 316 (ASS) | | SS 302<br>SS 304<br>SS 410<br>SS 430<br>(ASS) |
| | 15% | 60 | | | SS 302<br>SS 304<br>SS 316<br>SS 410<br>SS 430<br>(ASS) |
| | Up to 40% | 40 | uPVC<br>PE<br>PP<br>NR<br>NBR<br>IIR<br>EPDM<br>CR<br>FPM<br>CSM (GF) | | POM (GF) |
| | Up to 40% | 60 | PE<br>PP<br>IIR<br>EPDM<br>CR<br>FPM<br>CSM (GF) | uPVC<br>NR (GF) | POM<br>NBR (GF) |
| | 50% | 49 | PP (TPS 1978) | | |
| | 50% | 60 | PVC (TPS 1978) | | |
| | 50% | 66 | | PP (TPS 1978) | |
| | 50% | 85 | CPVC (TPS 1978) | | |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | 50% | 100 | | CPVC (TPS 1978) | |
| | 50% | 20 | | SS 316 (ASS) | SS 302<br>SS 304<br>SS 410<br>SS 430<br>(ASS) |
| | 50% | Boiling | | | SS 302<br>SS 304<br>SS 316<br>SS 410<br>SS 430<br>(ASS) |
| | 50% | | CSM (GPP) | | NR<br>SBR<br>CR<br>NBR<br>IIR<br>EPDM (GPP) |
| | 96% | 20 | uPVC (GF) | PE<br>PP<br>FPM (GF) | POM<br>NR<br>NBR<br>IIR<br>EPDM<br>CR<br>CSM (GF) |
| | 96% | 60 | | uPVC<br>PE (GF) | PP<br>POM<br>NR<br>NBR<br>IIR<br>EPDM<br>CR<br>FPM<br>CSM (GF) |
| | 98% | 22 | | | PVC<br>CPVC |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | | | | | (TPS 1978) |
| | 98% | 49 | | PP (TPS 1978) | |
| | 98% | 66 | PVDF (TPS 1978) | | PP (TPS 1978) |
| | 98% | 121 | | | PVDF (TPS 1978) |
| | 100% | 22 | | | PVC<br>CPVC (TPS 1978) |
| | 100% | 23 | | PP (TPS 1978) | |
| | 100% | 49 | | | PP (TPS 1978) |
| | Concentrated | | | | NR<br>SBR<br>CR<br>NBR<br>IIR<br>CSM<br>Si<br>EPDM (GPP) |
| | Concentrated | 20 | SS 302<br>SS 304<br>SS 316<br>SS 410<br>SS 430 (ASS) | | |
| | Concentrated | 40 | SS 316 (ASS) | SS 302<br>SS 304 (ASS) | SS 410<br>SS 430 (ASS) |
| | Concentrated | 60 | | SS 302<br>SS 304<br>SS 316 (ASS) | SS 410<br>SS 430 (ASS) |
| | Concentrated | 100 | | | SS 302<br>SS 304<br>SS 316 (ASS) |

TABLE 8 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

| Application | Chemical | | Material of Construction | | |
|---|---|---|---|---|---|
| | Conc. | Temp. (°C) | Recommended | Conditional | Not Recommended |
| | Oleum (100%) | 24 to 260 | Glass (CDS 1967) | | |

TABLE 9 MATERIALS OF CONSTRUCTION

| Abbreviation | Material of Construction |
|---|---|
| ABS | Acrylonitrile Butadiene Styrene |
| | Aluminum |
| CFE | Polychlorotrifluoroethylene (Plaskon, CTFE, KEL-F, Florothene) |
| CI | Cast Iron, Austenitic |
| | Cast Iron, High Silicone |
| | Chlorinated Polyether |
| CPVC | Chlorinated Polyvinyl Chloride |
| CR | Polychloroprene (Neoprene) |
| CS | Carbon Steel |
| CSM | Chlorosulphonated Polyethylene (Hypalon) |
| EPDM | Ethylene Propylene Rubber |
| FPM | Fluorine Rubber (Viton) |
| | Glass |
| | Iron |
| IIR | Isobutylene/Isoprene Rubber (Butyl) |
| | Lead |
| NBR | Acrylonitrile/Butadiene Rubber (Nitrile, Buna N) |
| NR | Natural Rubber |
| | Nickel |
| | Nickel-Copper Alloy (Monel) |
| PE | Polyethylene |
| POM | Polyoxymethylene |

TABLE 9 MATERIALS OF CONSTRUCTION (Cont'd)

| Abbreviation | Material of Construction |
|---|---|
| PP | Polypropylene |
| | Porcelain |
| PTFE | Polytetrafluoroethylene (Teflon) |
| PVC (Followed by grade, if any) | Polyvinyl Chloride |
| PVDC | Polyvinylidene Chloride (Saran) |
| PVDF | Polyvinylidene Fluoride |
| Si | Silicone |
| SBR | Styrene/Butadiene (GR-5, Buna S) |
| SS (Followed by grade) | Stainless Steel |
| | "20" Alloy (Durimet 20, Carpenter 20) |
| uPVC | Unplasticised Polyvinyl Chloride |
| | Wood |

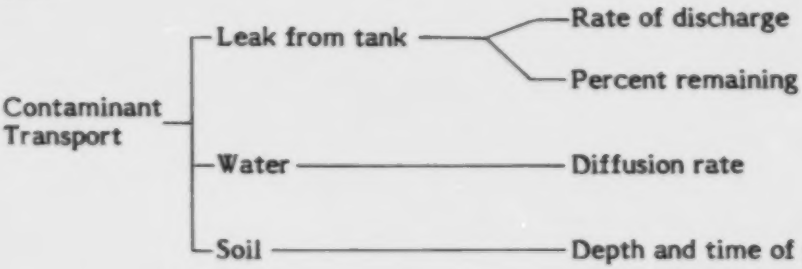
# 5 CONTAMINANT TRANSPORT

## 5.1 General Summary

Sulphuric acid is commonly transported in tank cars as a liquid. When spilled in water, it will mix slowly; oleum or concentrated acid solutions react violently. When spilled on soil, the liquid will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may cause environmental concerns.

Because sulphuric acid is essentially nonvolatile, dispersion in air is not a problem.

The following factors are considered for the transport of a spill in water and soil:




It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and, to some extent, inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

## 5.2 Leak Nomograms

**5.2.1 Introduction.** Sulphuric acid is commonly transported in railway tank cars as a nonpressurized liquid. While the capacities of the tank cars vary widely, one tank car size has been chosen for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80,000 L.

If a tank car loaded with sulphuric acid is punctured on the bottom, all of the contents will drain out by gravity. The aim of the nomograms is to provide a simple means to obtain the time history of the conditions in the tank car and the discharge rate

of the liquid. Because of the relatively low volatility of sulphuric acid and the fact that the tank cars are not pressurized, no leak nomograms have been prepared for vapour release from a puncture in the top of the tank.

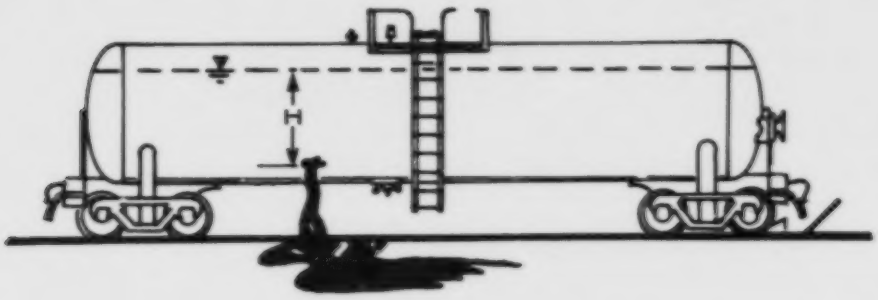



FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM

The rate of outflow (q) from a puncture hole in the bottom of the tank car is defined by the standard orifice equation (Streeter 1971). It is a function of the hole size (A) and shape, the height of the fluid above the puncture hole (H) and a coefficient of discharge (Cd).

As the gravitational force predominates over viscous and other forces for a wide range of fluid conditions, the rate of discharge is relatively independent of fluid temperature and viscosity. Consequently, it is reasonable to assume a constant discharge coefficient for sulphuric acid for a wide range of temperature and viscosity. For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

### 5.2.2 Nomograms.

**5.2.2.1 Figure 8: Percent remaining versus time.** Figure 8 provides a means of estimating the percent of liquid remaining in the standard tank car after the time of rupture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car (2.75 m $\phi$ x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80,000 L of sulphuric acid. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

FIGURE 8

SULPHURIC ACID

**PERCENT REMAINING VS TIME**

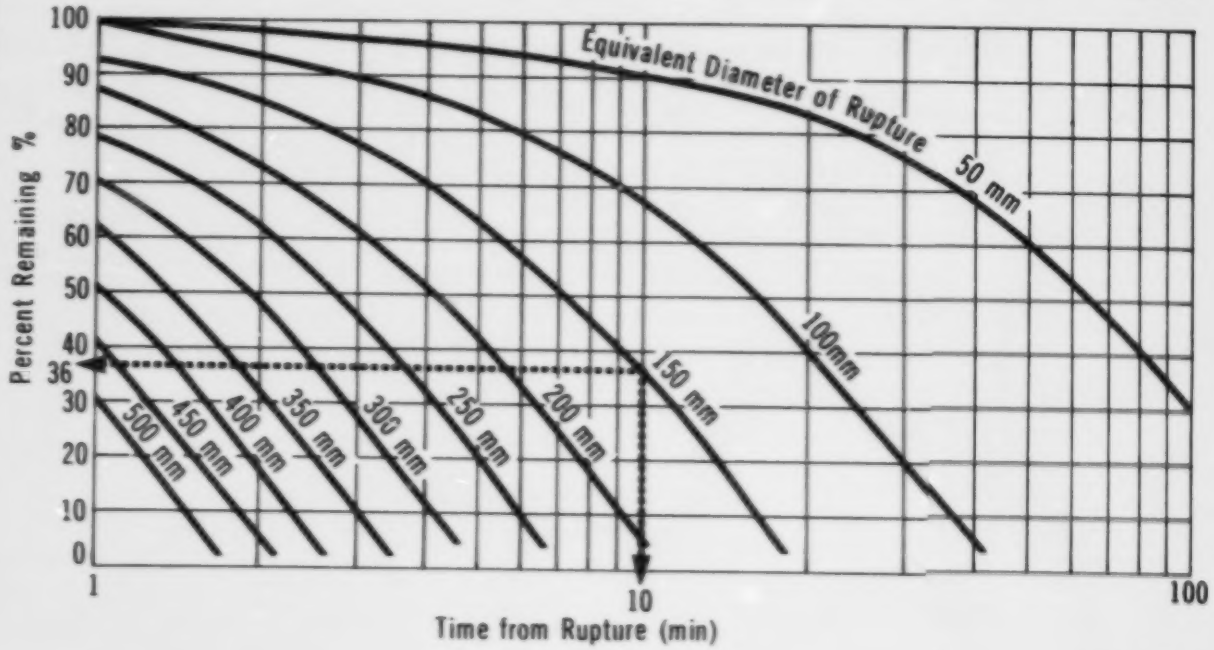
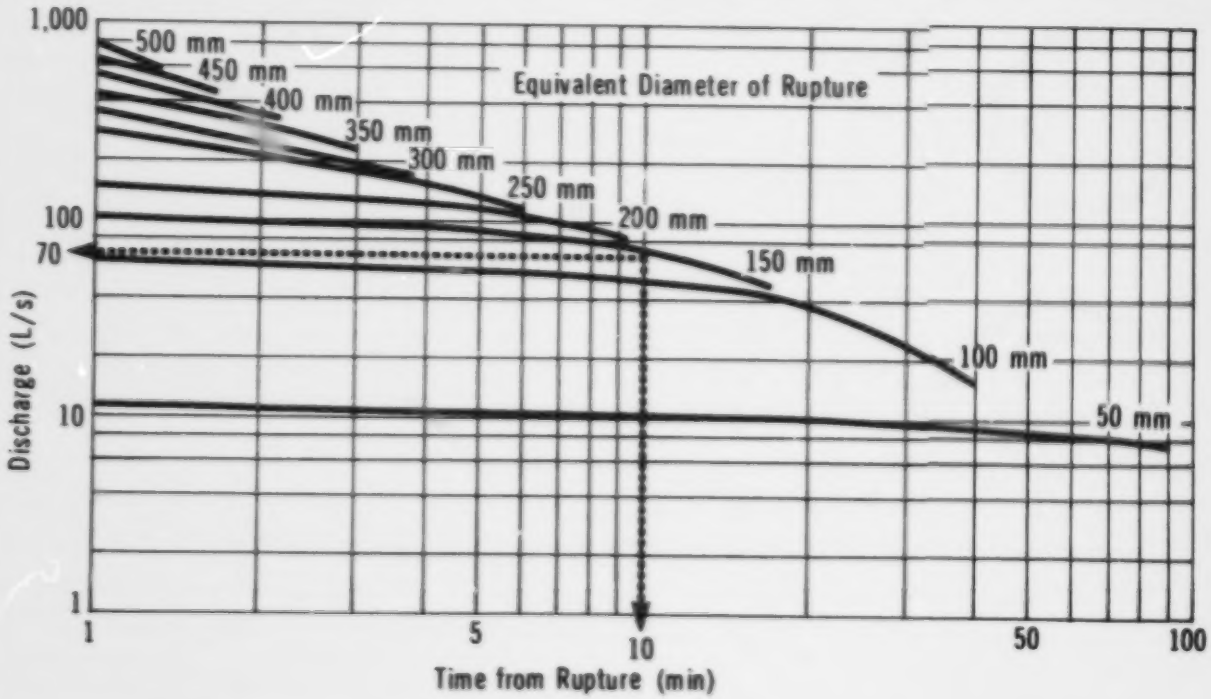



FIGURE 9

SULPHURIC ACID

**DISCHARGE RATE VS TIME**



5.2.2.2 **Figure 9: Discharge rate versus time.** Figure 9 provides a means of estimating the instantaneous discharge rate (L/s) at any time (t) after the time of rupture for a number of equivalent hole diameters. The nomogram is only applicable to the standard tank car size with an initial volume of 80,000 L.

**5.2.3 Sample Calculations.**

i) Problem A

The standard tank car (2.75 m Ø x 13.4 m long) filled with sulphuric acid has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80,000 L remains after 10 minutes?

Solution to Problem A

- Use Figure 8
- With t=10 min and d=150 mm, the amount remaining is about 36 percent or 28,800 L

ii) Problem B

With the same conditions as Problem A, what is the instantaneous discharge rate from the tank 10 minutes after the accident?

Solution to Problem B

- Use Figure 9
- With t=10 min and d=150 mm, the instantaneous discharge rate (q) = 70 L/s

**5.3 Dispersion in the Air**

5.3.1 **Introduction.** Since sulphuric acid is a nonvolatile liquid, direct venting of the vapour to the atmosphere from a hole in a ruptured vessel does not constitute a significant hazard downwind. However, oleum (30% or more excess $SO_3$) will release $SO_3$ vapour from a liquid pool spilled on a ground or water surface; therefore, this situation is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 10 depicts schematically the contaminant plume configuration from a continuous surface release. The dispersion model represents the liquid pool area source as a virtual point source (with the same vapour emission rate, Q) located 10 equivalent pool radii upwind.

When oleum (30% or more excess $SO_3$) is instantaneously spilled on land or water, $SO_3$ vapour will be released to the atmosphere. The $SO_3$ vapour released will react quickly with atmospheric water vapour to form sulphuric acid which will then nucleate and grow into an acid mist. The air dispersion nomograms presented here apply to dispersion of vapour releases and are not applicable to dispersion of mists, unless the particle size distribution of the mist is such that the mist is easily transported downwind. This would occur if all particles were less than 20 $\mu$m in diameter.

For spills on water, small-scale laboratory experiments have shown that sulphuric acid mist particles generated as a result of a spill of oleum (20% excess $SO_3$) were all less than 10 $\mu$m in diameter (Tang et al. 1982) and therefore can be easily transported downwind. However, due to dilution of the oleum with the water, it was conservatively estimated that no more than 0.1 percent of the spilled oleum would become airborne to form an acid mist under most spill conditions on water. On land, however, dilution with water may not occur and considerably more $SO_3$ vapour would be released to the atmosphere. Therefore, for conservative purposes it will be assumed that all of the free $SO_3$ content from a spill of oleum (30% or more excess $SO_3$) will form sulphuric acid mist that will behave as a vapour. This will result in conservative estimations for spills on land; however, for spills on water, grossly over-estimated results will be obtained.

**5.3.2 Vapour Dispersion Nomograms and Tables.** The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

Figure 12: vapour emission rate from a liquid pool as a function of maximum pool radius for various temperatures

Table 10: weather conditions

Figure 13: normalized vapour concentration as a function of downwind distance and weather conditions

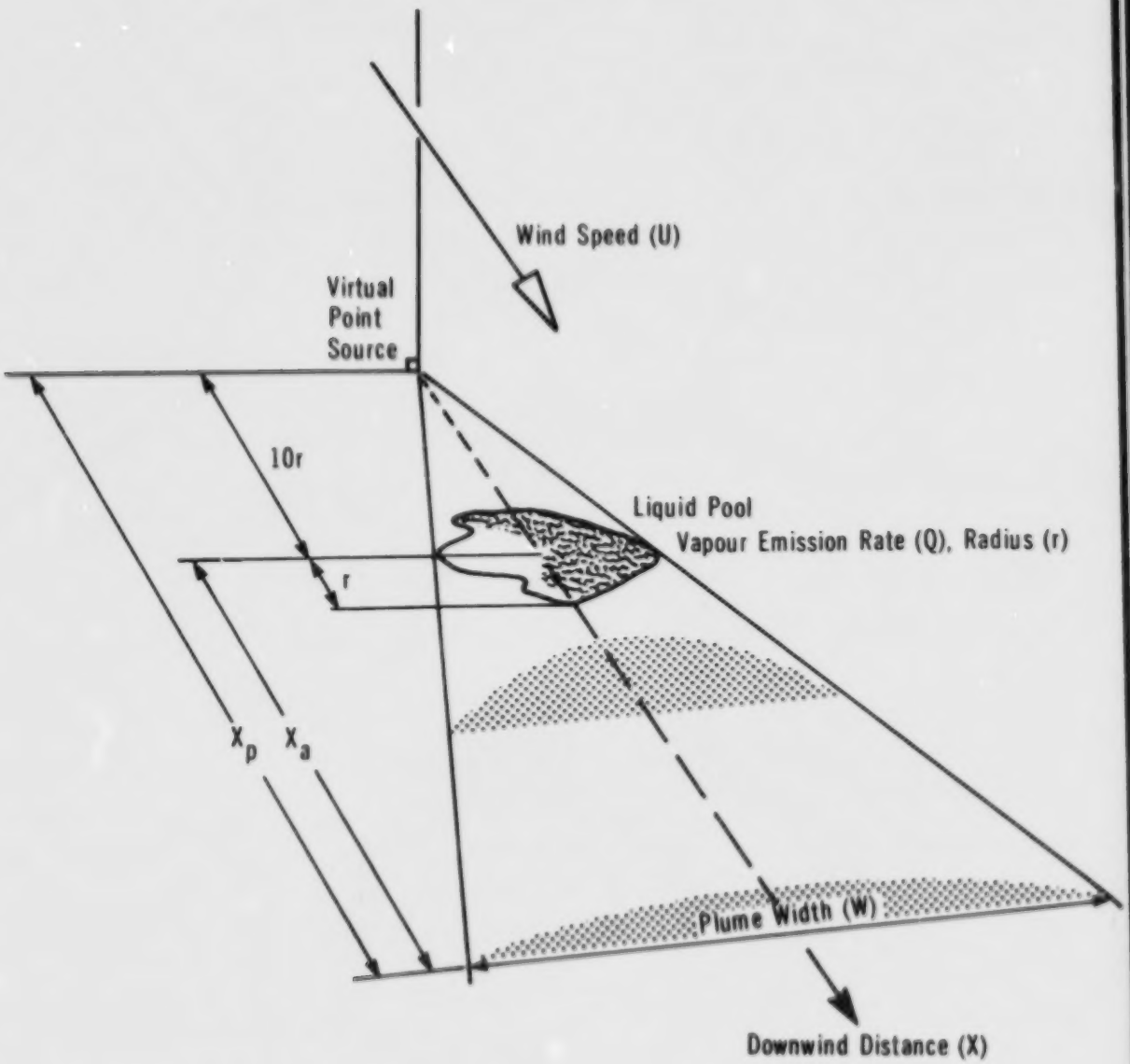
Table 11: maximum plume hazard half-widths

Figure 14: vapour plume travel distance as a function of time elapsed since the spill and wind speed

FIGURE 10

SULPHURIC ACID

## SCHEMATIC OF CONTAMINANT PLUME



The flow chart given in Figure 11 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" are contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

**5.3.2.1 Figure 12: Vapour emission rate versus liquid pool radius for various temperatures.** An evaporation rate for sulphuric acid (as $SO_3$ vapour from oleum) has been calculated employing the evaporation rate equations contained in the Introduction Manual. The computed evaporation rate for oleum at 20°C and a wind speed of 4.5 m/s (16.1 km/h) is 0.26 $g/m^2s$. Evaporation rates at other temperatures have been calculated using the evaporation rate equation which, at a given wind speed, is dependent on ambient temperature and the vapour pressure (CRC 1980) of oleum at that temperature. For example, evaporation rates of 0.053 $g/m^2s$ at 0°C and 0.56 $g/m^2s$ at 30°C were calculated for a wind speed of 4.5 m/s. Note that in an actual spill situation, $SO_3$ vapour released from a liquid pool will lower the concentration of free $SO_3$ in the liquid phase and result in lower $SO_3$ evaporation rates with time. The use of the value at the initial free $SO_3$ concentration will therefore be the worst case situation.

Using a 2 mm pool depth, the maximum spill radius corresponding to various spill amounts of oleum may be determined. The resultant spill areas and the oleum evaporation rates provide the basis for preparation of the vapour release rate versus spill radius nomogram in Figure 12.

Use: For a pool of oleum of known radius, the rate (Q) at which oleum vapour is released to the atmosphere at a given temperature can then be estimated from Figure 12. The solid portions of the curves represent spills of 0.1 to 156 tonnes, the latter representing about one standard 80,000 L (17,600 Imp. gal.) rail car load of oleum. It should be noted that Figure 12 is valid for a wind speed of 4.5 m/s (16.1 km/h) and therefore can only be used to provide an approximation of oleum vapour emission rates at other wind speeds. The Introduction Manual contains the appropriate equation to convert the evaporation rate at 4.5 m/s to an evaporation rate at another wind speed should it be desired.

It should also be noted that the determination of the emission rate is based on an arbitrary spill radius on flat land. The spill radius for any given spill amount was calculated assuming a 2 mm depth of spill value and assuming symmetrical spreading of the spilled liquid. The resultant spill radius is considered to provide the maximum value,

FIGURE 11

SULPHURIC ACID

## FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE

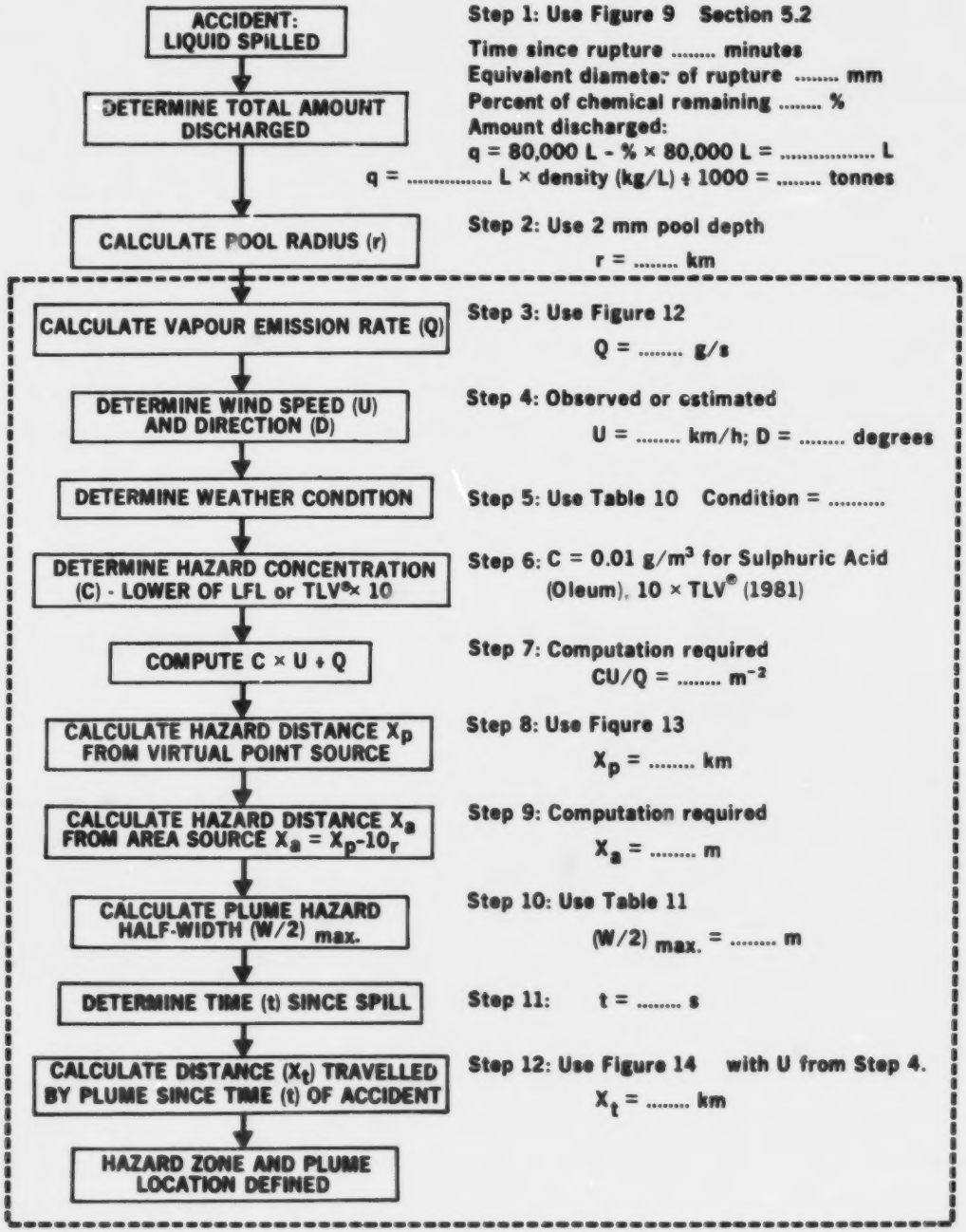
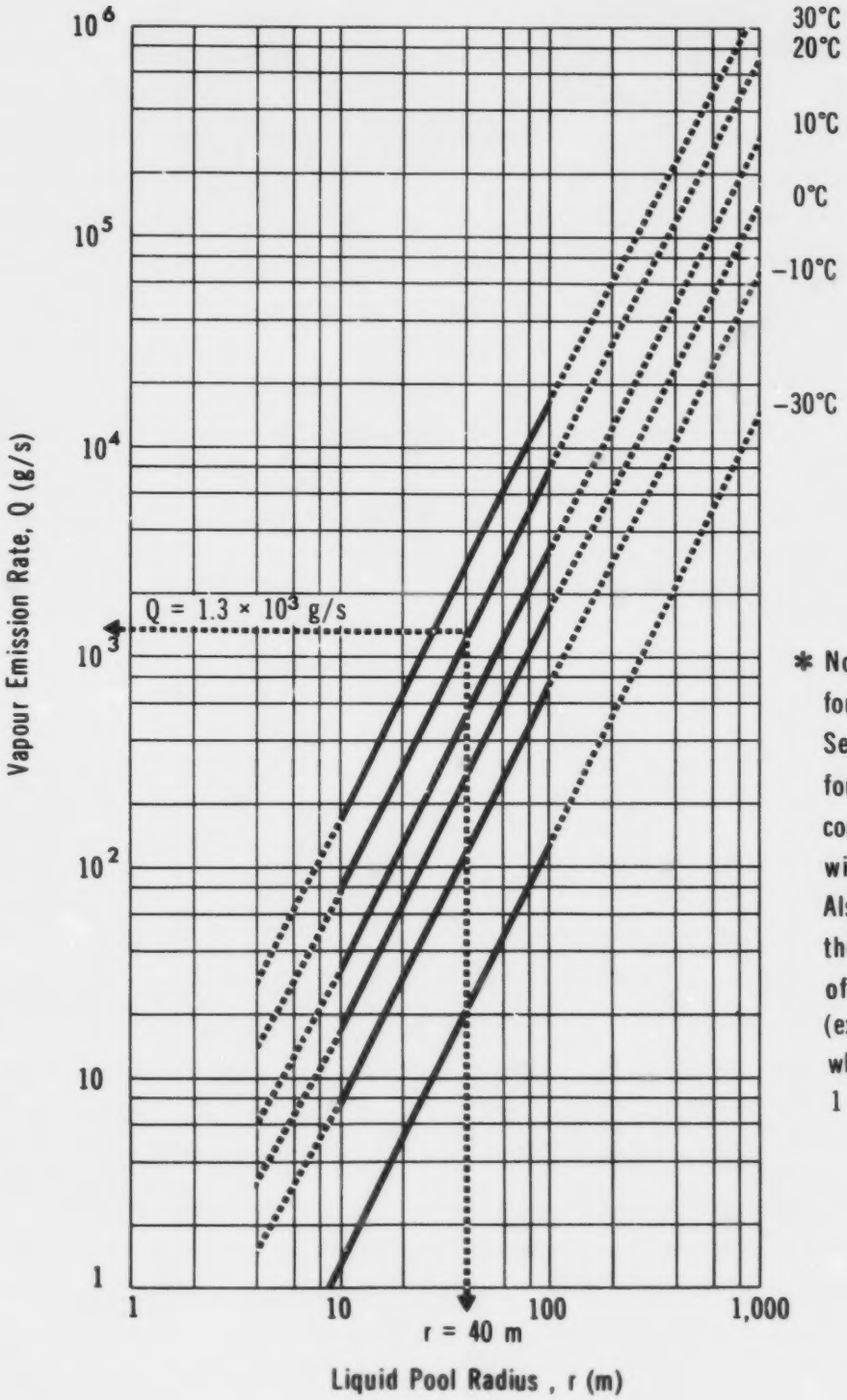

ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
CALCULATE POOL RADIUS (r)
CALCULATE VAPOUR EMISSION RATE (Q)
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C × U ÷ Q
CALCULATE HAZARD DISTANCE $X_p$ FROM VIRTUAL POINT SOURCE
CALCULATE HAZARD DISTANCE $X_a$ FROM AREA SOURCE $X_a = X_p - 10_r$
CALCULATE PLUME HAZARD HALF-WIDTH $(W/2)_{max.}$
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE ($X_t$) TRAVELLED BY PLUME SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PLUME LOCATION DEFINED
Step 1: Use Figure 9 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80,000 L - % × 80,000 L = ..... L
q = ..... L × density (kg/L) ÷ 1000 = ..... tonnes
Step 2: Use 2 mm pool depth
r = ..... km
Step 3: Use Figure 12
Q = ..... g/s
Step 4: Observed or estimated
U = ..... km/h; D = ..... degrees
Step 5: Use Table 10 Condition = .....
Step 6: C = 0.01 g/m³ for Sulphuric Acid (Oleum), 10 × TLV® (1981)
Step 7: Computation required
CU/Q = ..... m⁻²
Step 8: Use Figure 13
$X_p$ = ..... km
Step 9: Computation required
$X_a$ = ..... m
Step 10: Use Table 11
$(W/2)_{max.}$ = ..... m
Step 11: t = ..... s
Step 12: Use Figure 14 with U from Step 4.
$X_t$ = ..... km

FIGURE 12

SULPHURIC ACID

**VAPOUR EMISSION RATE VS LIQUID POOL RADIUS FOR VARIOUS TEMPERATURES**




* Note: Nomogram applies for wind speed of 4.5 m/s. See Introduction Manual for relationships to compute values for other wind speeds, if necessary. Also, the solid portions of the curves represent spills of 0.1 to 156 tonnes. (except −30°C and −10°C, where lower limit is 1 tonne)

since the type of ground surface that would normally be encountered in a spill situation (namely, irregular and porous) would likely cause a smaller observed spill radius.

**5.3.2.2 Figure 13: Vapour concentration versus downwind distance.** Figure 13 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (CU/Q) at the centreline of the contaminant plume. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 13, the weather condition must be determined from Table 10.

TABLE 10 WEATHER CONDITIONS

| Weather Condition F | Weather Condition D |
|---|---|
| Wind speed <11 km/h (< 3 m/s) and one of the following:<br>- overcast day<br>- night time<br>- severe temperature inversion | Most other weather conditions |

Use: The maximum hazard distance, $X_p$, downwind of the spill can be calculated from Figure 13 knowing:

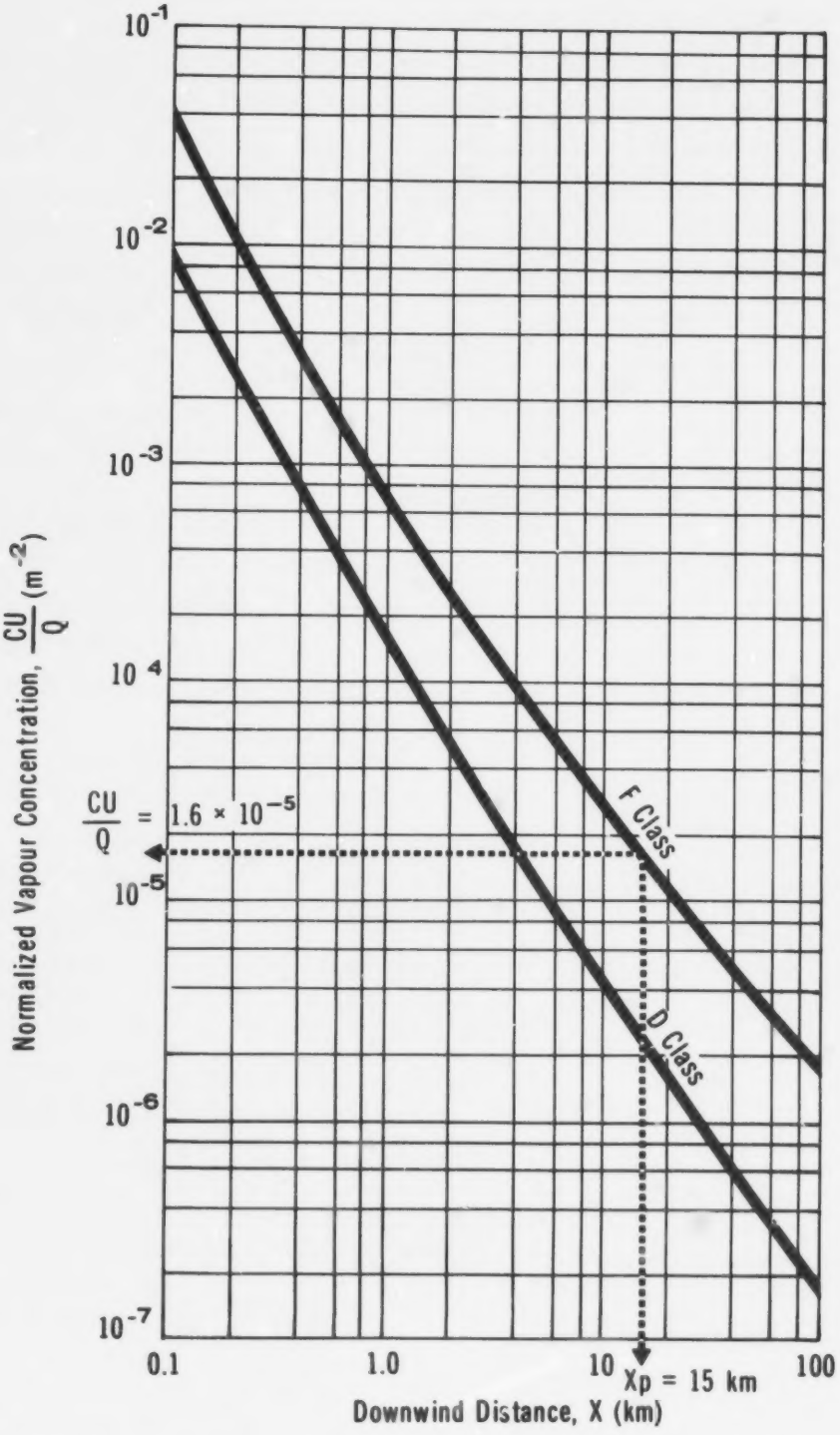
- Q, the vapour emission rate (g/s)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value• (TLV in $g/m^3$), or the Lower Flammability Limit (LFL in $g/m^3$), which for nonflammable vapour will be 10 x TLV•. Note that the TLV• for sulphuric acid (oleum) is provided only in $g/m^3$ and is not pertinent in ppm. Therefore, a conversion nomogram (from ppm to $g/m^3$) is not provided.

A hazard concentration limit of 10 times the TLV• has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e. on the order of 30 minutes). The TLV• is a workplace standard for

FIGURE 13

SULPHURIC ACID

**NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE**



long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

**5.3.2.3 Table 11: Maximum plume hazard half-widths.** This table presents data on the maximum plume hazard half-width, $(W/2)_{max}$, for a range of Q/U values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the oleum Threshold Limit Value (TLV•) of 0.001 g/m$^3$, or 0.01 g/m$^3$. The maximum plume hazard half-width represents the maximum half-width of the oleum vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV•. Table 11 is therefore only applicable for an oleum hazard concentration limit of 10 x TLV• or 0.01 g/m$^3$. Also, data are provided up to a maximum hazard distance downwind of 100 km.

TABLE 11 MAXIMUM PLUME HAZARD HALF-WIDTHS (FOR SULPHURIC ACID (OLEUM) AT 20°C)

| Weather Condition D | | | Weather Condition F | | |
|---|---|---|---|---|---|
| Q/U (g/m) | $(W/2)_{max}$ (m) | | Q/U (g/m) | $(W/2)_{max}$ (m) | |
| 70,000 | 3,430 | (99.5 km*) | 6,000 | 1,430 | (99.5 km*) |
| 60,000 | 3,115 | | 5,000 | 1,250 | |
| 50,000 | 2,785 | | 4,000 | 1,060 | |
| 40,000 | 2,425 | | 3,000 | 855 | |
| 30,000 | 2,030 | | 2,000 | 630 | |
| 25,000 | 1,815 | | 1,000 | 380 | |
| 20,000 | 1,580 | | 750 | 310 | |
| 15,000 | 1,320 | Q/U = 619 → | 500 | 240 | → $(W/2)_{max}$ = 275 m |
| 10,000 | 1,030 | | 250 | 155 | |
| 7,500 | 860 | | 100 | 85 | |
| 5,000 | 670 | | 50 | 55 | |
| 2,500 | 450 | | 25 | 35 | |
| 1,000 | 260 | | 10 | 25 | |
| 750 | 220 | | | | |
| 500 | 175 | | *Data are provided up to a maximum downwind hazard distance of 100 km. | | |
| 250 | 115 | | | | |
| 100 | 70 | | | | |
| 50 | 45 | | | | |
| 10 | 20 | | | | |

Example: A spill releasing oleum vapour at the rate of Q = 1.3 x 10$^3$ g/s under weather condition F and a wind speed U = 2.1 m/s means Q/U = 619 g/m which results in a maximum plume hazard half-width $(W/2)_{max}$ = 275 m.

Note: Above table is valid only for an oleum concentration of 10 x TLV•, or 0.01 g/m$^3$.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of vapour emission rates (Q) used was 300 to 70,000 g/s, corresponding to oleum spills in the range of about 5 to 1,100 tonnes, respectively. If the entire contents of an 80,000 L (17,600 Imp. gal.) tank car spill, the mass spilled would be 156,000 kg or approximately 156 tonnes. Therefore, under class D of Table 11, data are provided for up to 7 times this amount.

Under weather condition F, the wind speed (U) range applicable is up to 3 m/s. The range of vapour emission rates (Q) used was 30 to 6,000 g/s, corresponding to oleum spills in the range of about 0.05 to 90 tonnes, respectively. Therefore, under class F of Table 11, data are provided for only up to about 60 percent of a standard rail car load.

Use: Knowing the weather condition, Q and U, compute Q/U. Choose the closest Q/U value in the table and the corresponding $(W/2)_{max}$, the maximum plume hazard half-width, in metres. (For a slightly more accurate number, interpolate Q/U and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 11.

**5.3.2.4 Figure 14: Plume travel time versus travel distance.** Figure 14 presents plots of plume travel time (t) versus plume travel distance ($X_t$) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance ($X_t$), which indicates how far downwind the plume has travelled, can be determined.

**5.3.3 Sample Calculation.** The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid oleum. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e of the spill radius) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of oleum were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

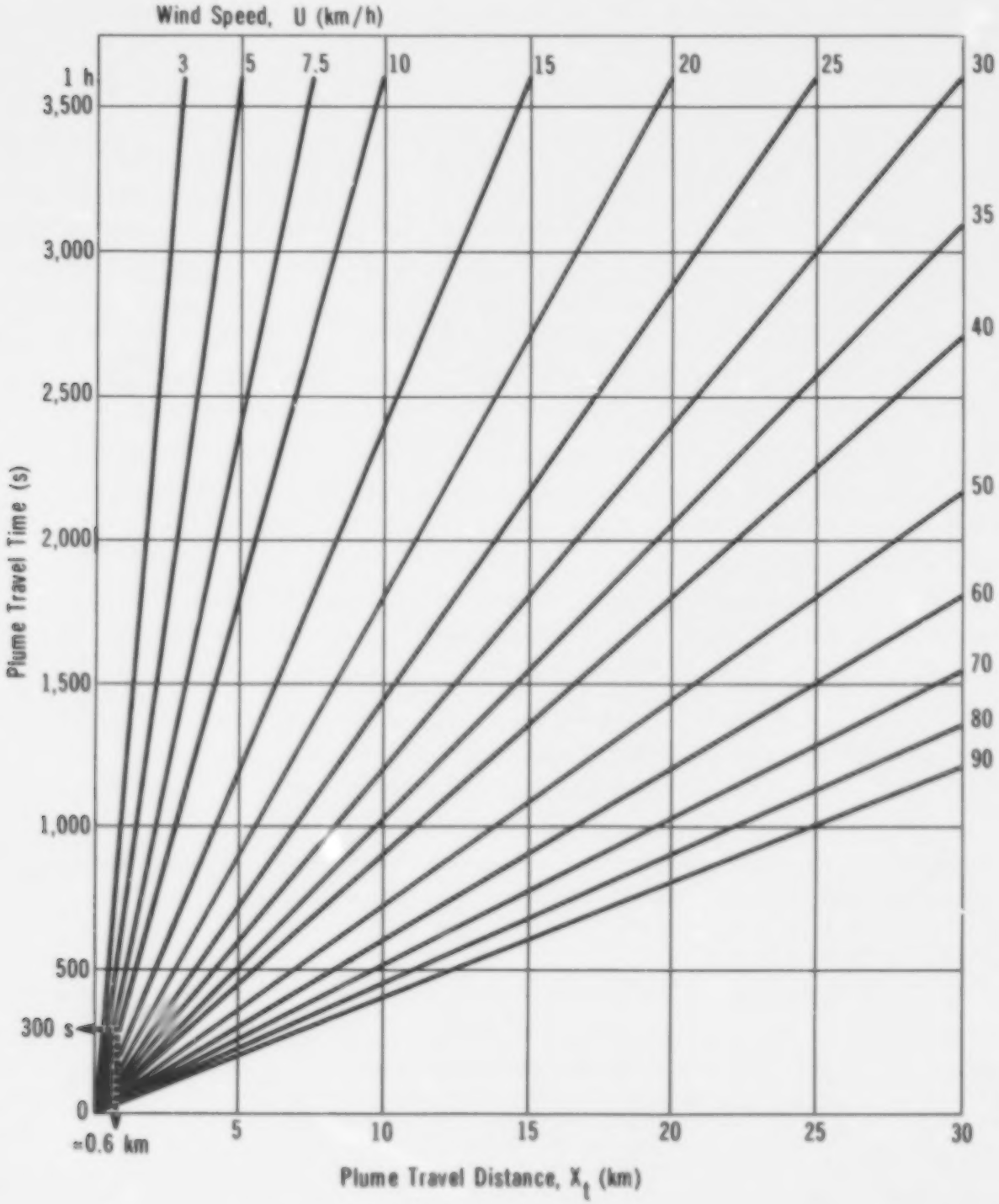
Solution

Step 1: Quantity spilled is given, 20 tonnes

FIGURE 14

SULPHURIC ACID

**PLUME TRAVEL TIME VS TRAVEL DISTANCE**



Step 2: Determine pool radius (r) for spill of 20 tonnes

- Use observed (measured) pool radius if possible. If not, use a 2 mm pool depth: $r(m) = \sqrt{\text{Volume}/\pi \text{ depth}}$
- Radius (r) = 40 m ÷ 1,000 = 0.04 km, here $r(m) = \sqrt{\frac{V(\text{tonnes})}{0.012}}$

Step 3: Calculate vapour emission rate (Q) at T = 20°C

- From Figure 12, r = 40 m and T = 20°C
- $Q = 1.3 \times 10^3$ g/s

Step 4: Determine wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given:

  U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s

  D = NW or 315° (D = Direction from which wind is blowing)

Step 5: Determine weather condition

- From Table 10, weather condition = F since U is less than 11 km/h and it is night

Step 6: Determine hazard concentration limit (C)

- This is the lower of 10 times the TLV®, or the LFL; since oleum vapours are not flammable, this is 10 x TLV®
- $C = 0.01$ g/m$^3$ (TLV® = 0.001 g/m$^3$; no LFL)

Step 7: Compute CU/Q

- $CU/Q = \frac{0.01 \times 2.1}{1.3 \times 10^3} = 1.6 \times 10^{-5}$ m$^{-2}$

Step 8: Calculate downwind distance ($X_p$) from the virtual point source

- From Figure 13 with CU/Q = $1.6 \times 10^{-5}$ m$^{-2}$ and weather condition F, $X_p \approx 15$ km

Step 9: Calculate hazard distance ($X_a$) downwind of the area source

- With $X_p$ = 15 km and r = 0.04 km then

  $X_a = X_p - 10\,r$ = 15 km - 10 (0.04 km) = 14.6 km

Step 10: Calculate plume hazard half-width $(W/2)_{max}$

- Use Table 11

- With $Q = 1.3 \times 10^3$ g/s and U = 2.1 m/s

  then $Q/U = \dfrac{1.3 \times 10^3}{2.1} = 619$ g/m

- Then for weather condition F the closest Q/U value is between 500 and 750 g/m which gives $(W/2)_{max} = 275$ m

Step 11: Determine the time since spill

- t = 5 min x 60 = 300 s

Step 12: Calculate distance travelled ($X_t$) by vapour plume since time of accident

- Using Figure 14 with t = 300 s and U = 7.5 km/h, then $X_t$ = 0.6 km (more accurately from Ut = 2.1 m/s x 300 s = 630 m = 0.63 km).

Step 13: Map the hazard zone.

- This is done by drawing a rectangular area with dimensions of twice the maximum plume hazard half-width (275 m) by the maximum hazard distance downwind of the area source (14.6 km) along the direction of the wind, as shown in Figure 15
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° $\pm$ 10°), the hazard zone is defined as shown in Figure 16
- Note that the plume has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h there remain 112 minutes before the plume reaches the maximum downwind hazard distance of 14.6 km

## 5.0 Behaviour in Water

**5.0.1 Introduction.** When spilled on water, sulphuric acid has often been observed to sink and slowly mix with the water. For purposes of this section, it will be presumed that sulphuric acid has already dissolved or mixed with the water. This mixing can generally be described by classical diffusion equations with one or more diffusion coefficients. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

To estimate pollutant concentration in a river downstream from a spill, the turbulent diffusion has been modelled. The model employed is strictly applicable to neutrally buoyant liquids and solids that dissolve in water. As sulphuric acid is denser than water, the maximum concentration would be expected near the bottom.

The one-dimensional model uses an idealized rectangular channel section and assumes a uniform concentration of the pollutant throughout the section. Obviously, this

FIGURE 15

SULPHURIC ACID

**HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM**

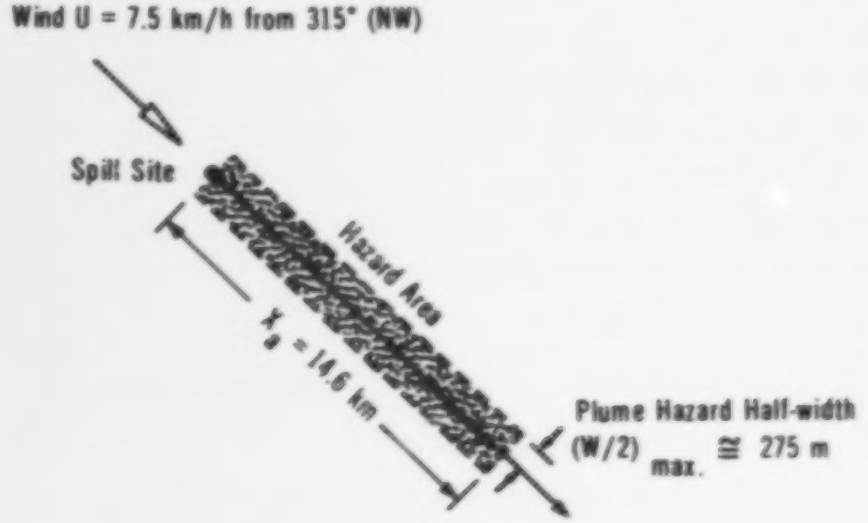
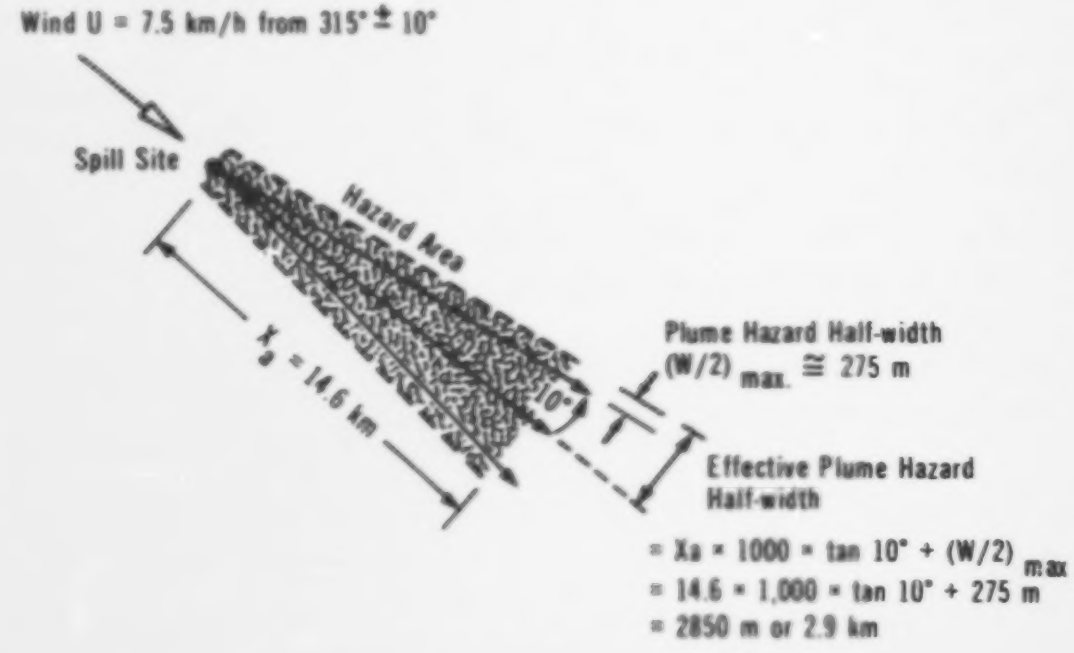



FIGURE 16

SULPHURIC ACID

**HAZARD AREA FOR UNSTEADY WINDS, EXAMPLE PROBLEM**


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
$X_a$ = 14.6 km
10°
Plume Hazard Half-width
$(W/2)_{max.} \cong$ 275 m
Effective Plume Hazard Half-width
= Xa × 1000 × tan 10° + $(W/2)_{max}$
= 14.6 × 1,000 × tan 10° + 275 m
= 2850 m or 2.9 km

applies only to points sufficiently far downstream of the spill where mixing and dilution have distributed the pollutant across the entire river channel. The model is applicable to rivers where the ratio of width to depth is less than 100 (W/d <100) and assumes a Manning's roughness coefficient of 0.03. Details of the model are outlined in the Introduction Manual.

No modelling has been carried out for molecular diffusion in still water. Rather, nomograms have been prepared to define the hazard zone and the average concentration within the hazard zone as a function of spill size, but independent of time.

5.4.2 **Nomograms.** The following nomograms are presented to calculate pollutant concentrations in non-tidal rivers and in lakes (still water).

Non-tidal Rivers

Figure 18: time versus distance for a range of average stream velocities

Figure 19: hydraulic radius versus channel width for a range of stream depths

Figure 20: diffusion coefficient versus hydraulic radius for a range of average stream velocities

Figure 21: alpha* versus diffusion coefficient for various time intervals

Figure 22: alpha versus delta* for a range of spill sizes

Figure 23: maximum concentration versus delta for a range of river cross-sectional areas

Lakes or Still Water Bodies

Figure 24: volume versus radius for the hazard zone for a range of lake depths

Figure 25: average concentration versus volume for the hazard zone for a range of spill sizes

The flow chart in Figure 17 outlines the steps required to estimate downriver concentration after a spill and identifies the nomograms to be used. These nomograms (Figures 18 through 23) are described in the following sub-sections.

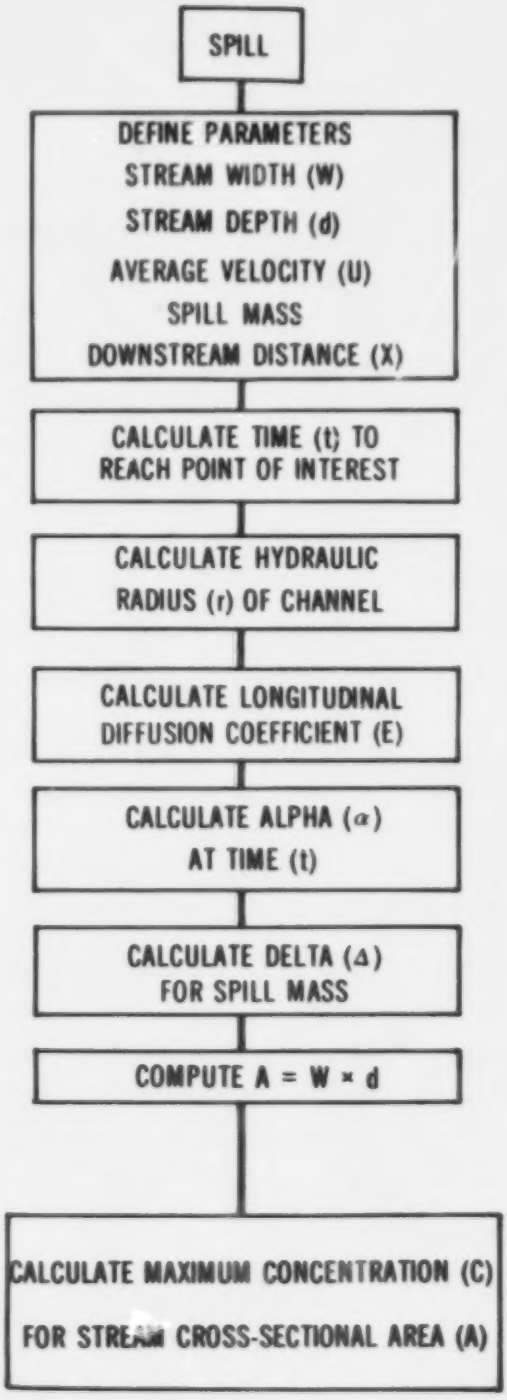
---

*Alpha and delta are conversion factors only and are of no significance other than to facilitate calculation of downstream concentrations.

FIGURE 17

SULPHURIC ACID

## FLOW CHART TO DETERMINE POLLUTANT CONCENTRATION IN NON-TIDAL RIVERS


SPILL
DEFINE PARAMETERS
STREAM WIDTH (W)
STREAM DEPTH (d)
AVERAGE VELOCITY (U)
SPILL MASS
DOWNSTREAM DISTANCE (X)
CALCULATE TIME (t) TO REACH POINT OF INTEREST
CALCULATE HYDRAULIC RADIUS (r) OF CHANNEL
CALCULATE LONGITUDINAL DIFFUSION COEFFICIENT (E)
CALCULATE ALPHA (α) AT TIME (t)
CALCULATE DELTA (Δ) FOR SPILL MASS
COMPUTE A = W × d
CALCULATE MAXIMUM CONCENTRATION (C) FOR STREAM CROSS-SECTIONAL AREA (A)

Step 1: Observed or Estimated

W = _____ m

d = _____ m

U = _____ m/s

MASS = _____ tonnes

X = _____ m

Step 2: Use Figure 18

t = _____ minutes

Step 3: Use Figure 19

r = _____ m

Step 4: Use Figure 20

E = _____ $m^2/s$

Step 5: Use Figure 21

$\alpha$ = _____

Step 6: Use Figure 22

$\Delta$ = _____

Step 7: Compute stream cross-sectional Area (A)

A = W × d _____ $m^2$

Step 8: Use Figure 23

C = _____ ppm

**5.4.2.1 Nomograms for non-tidal rivers.**

**Figure 18: Time versus distance.** Figure 18 presents a simple relationship between average stream velocity, time and distance. Using an estimate of average stream velocity (U), the time (t) to reach any point of interest at some distance (X) downstream of the spill can be readily obtained from Figure 18.

**Figure 19: Hydraulic radius versus channel width.** The model used to estimate downstream pollutant concentration is based on an idealized rectangular channel of width (W) and depth (d).

The hydraulic radius (r) for the channel is required in order to estimate the turbulent diffusion coefficient (E). The hydraulic radius (r) is defined as the stream cross-sectional area (A) divided by the wetted perimeter (P). Figure 19 is a nomogram for computation of the hydraulic radius (r) using the width and depth of the idealized river cross-section.

**Figure 20: Diffusion coefficient versus hydraulic radius.** Figure 20 permits calculation of the diffusion coefficient (E), knowing the hydraulic radius (r) from Figure 19 and the average stream velocity (U).

**Figure 21: Alpha versus diffusion coefficient.** Figure 21 is used to estimate a conversion factor alpha ($\alpha$), which is a function of the diffusion coefficient (E) and the time (t) to reach the point of interest downstream of the spill.

**Figure 22: Alpha versus delta.** A second conversion factor, delta ($\Delta$), must be estimated from Figure 22 to allow determination of pollutant concentration at the point of interest. Delta ($\Delta$) is a function of alpha ($\alpha$) and the spill mass.

**Figure 23: Maximum concentration versus delta.** Figure 23 represents the final step for calculation of the maximum downstream pollutant concentration (C) at the point of interest. Using the factor delta ($\Delta$) and knowing the stream cross-sectional area (A), the concentration (C) is readily obtained from the nomogram. The value obtained from Figure 23 applies to neutrally buoyant liquids or solids and will vary somewhat for other pollutants which are heavier or lighter than water.

**5.4.2.2 Nomograms for lakes or still water bodies.**

**Figure 24: Volume versus radius.** The spill of a neutrally buoyant liquid in a lake in the absence of wind and current has been idealized as a cylinder of radius (r) and length (d), equivalent to the depth of the lake at the point of spill. The volume of water

FIGURE 18

SULPHURIC ACID

## TIME vs DISTANCE

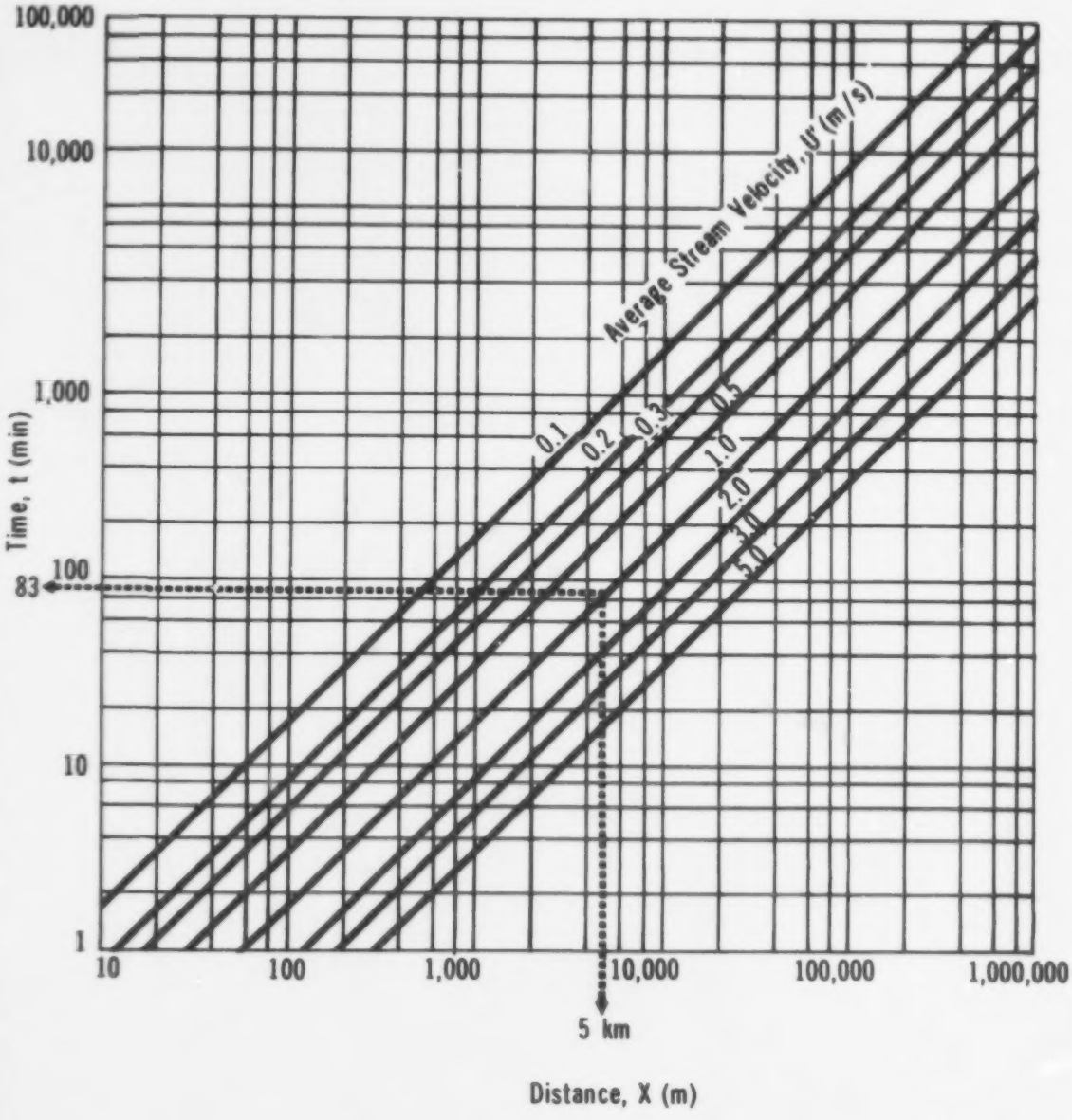


FIGURE 19

SULPHURIC ACID

HYDRAULIC RADIUS VS CHANNEL WIDTH

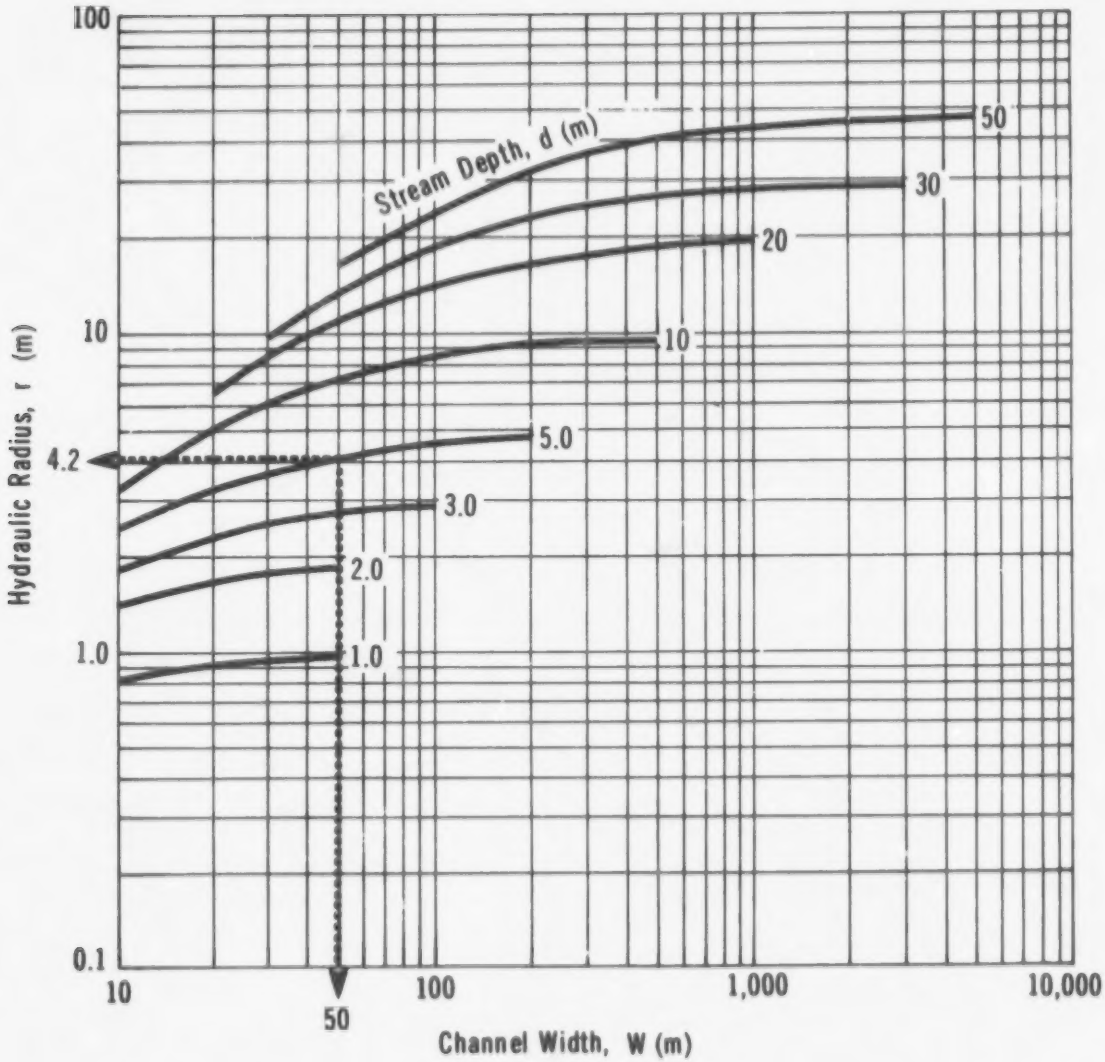


FIGURE 20

SULPHURIC ACID

DIFFUSION COEFFICIENT
VS HYDRAULIC RADIUS

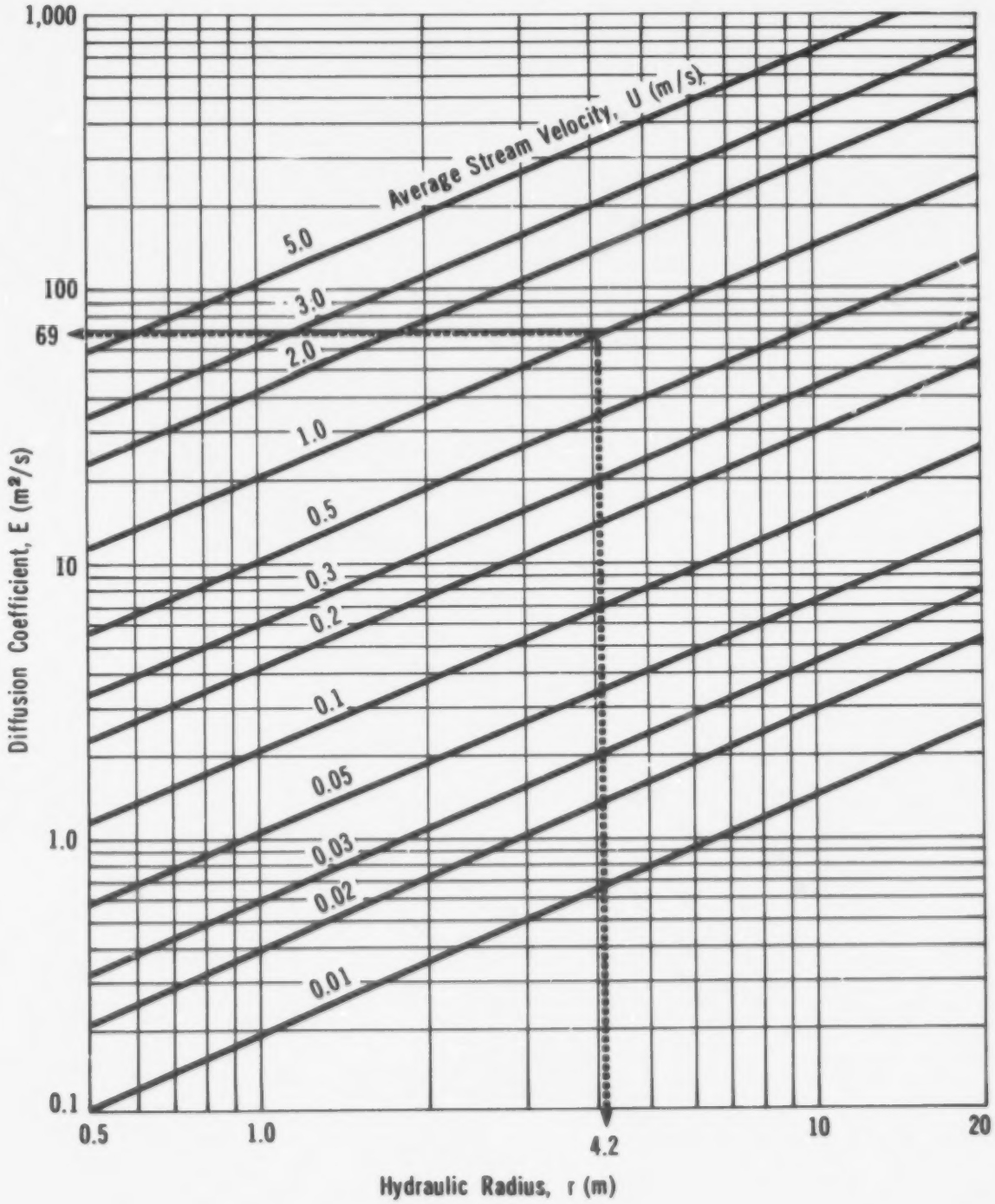


FIGURE 21

SULPHURIC ACID

## ALPHA vs DIFFUSION COEFFICIENT

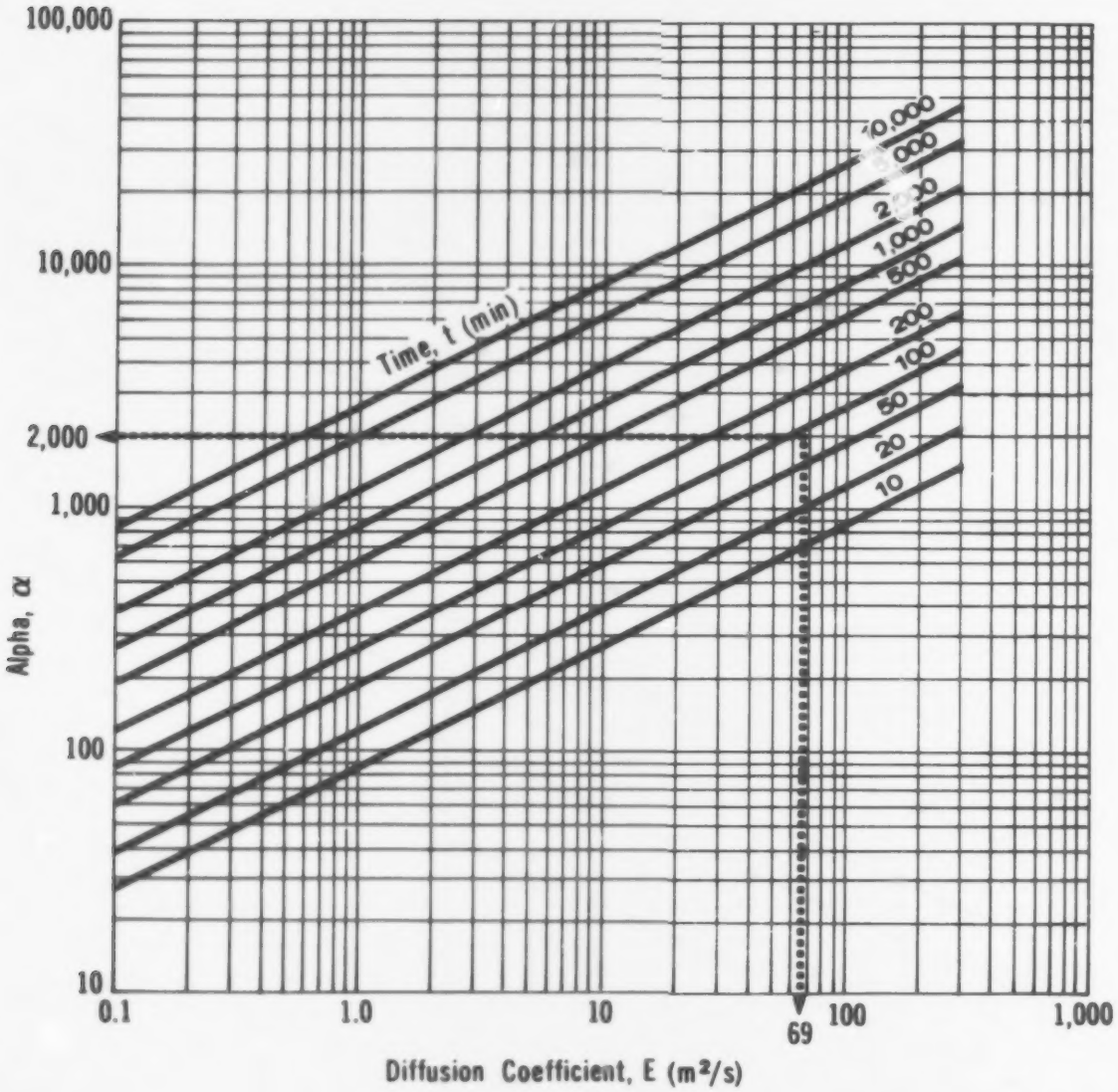


FIGURE 22

SULPHURIC ACID

## ALPHA vs DELTA

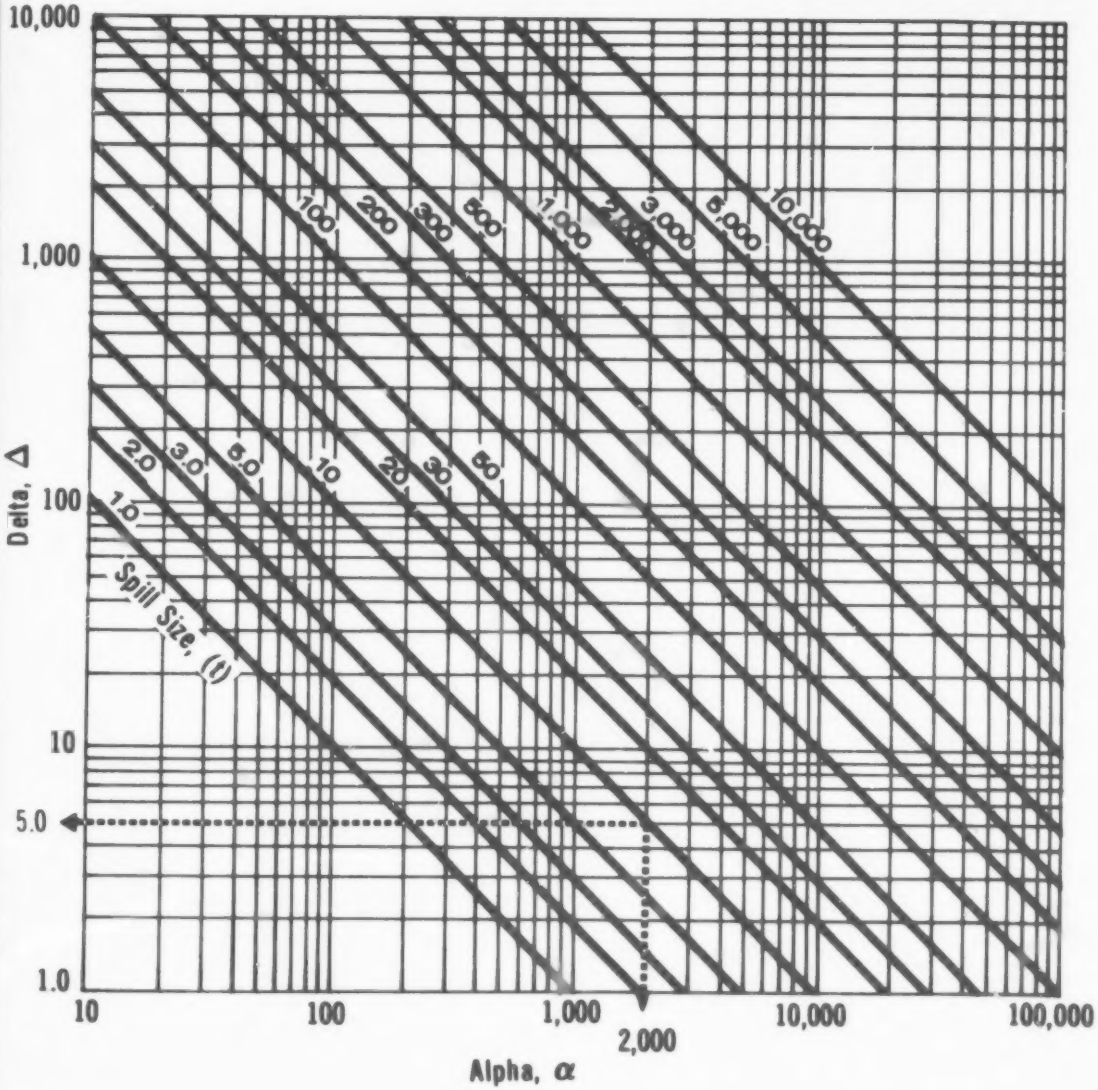


FIGURE 23

SULPHURIC ACID

## MAXIMUM CONCENTRATION vs DELTA

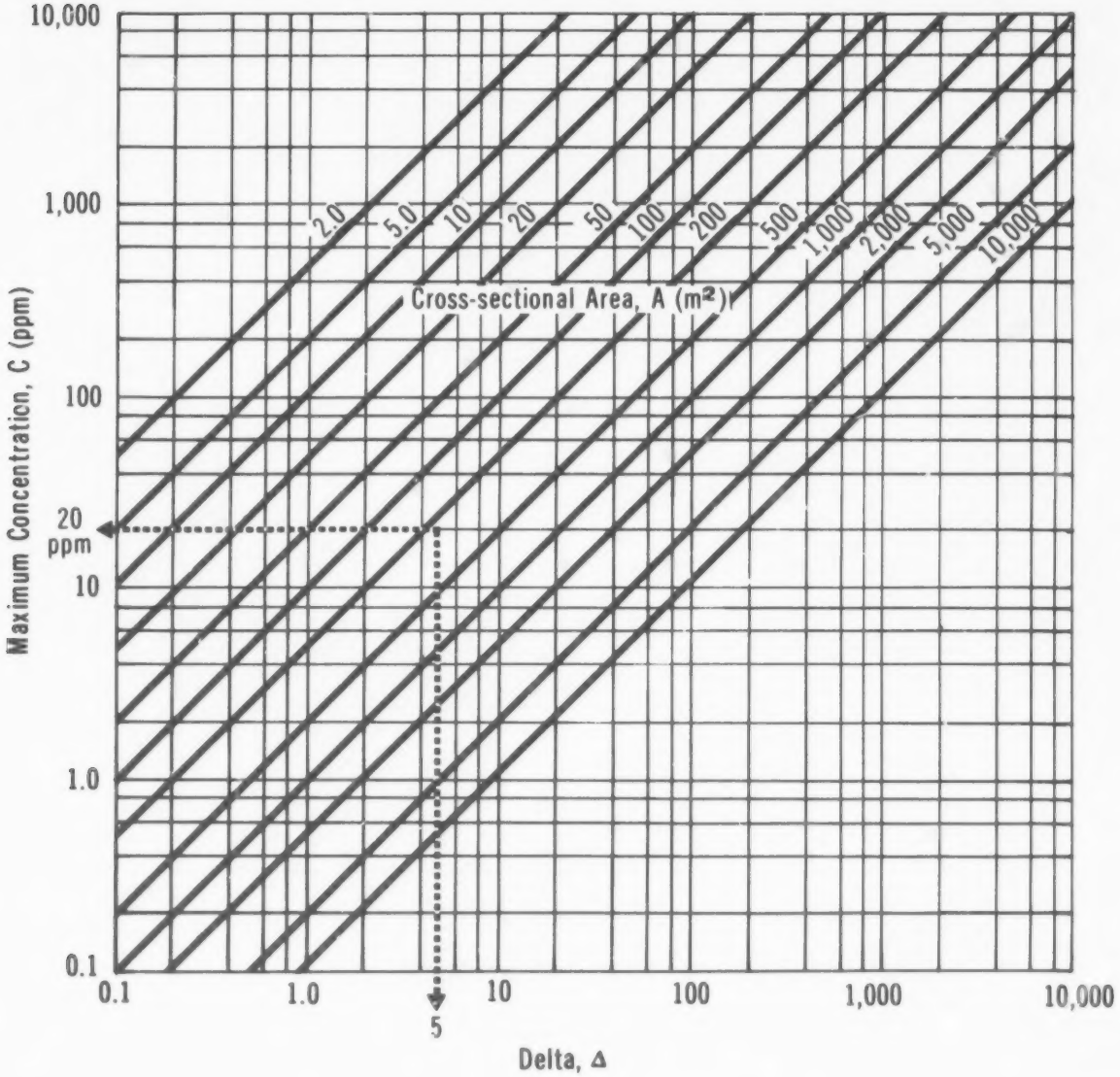
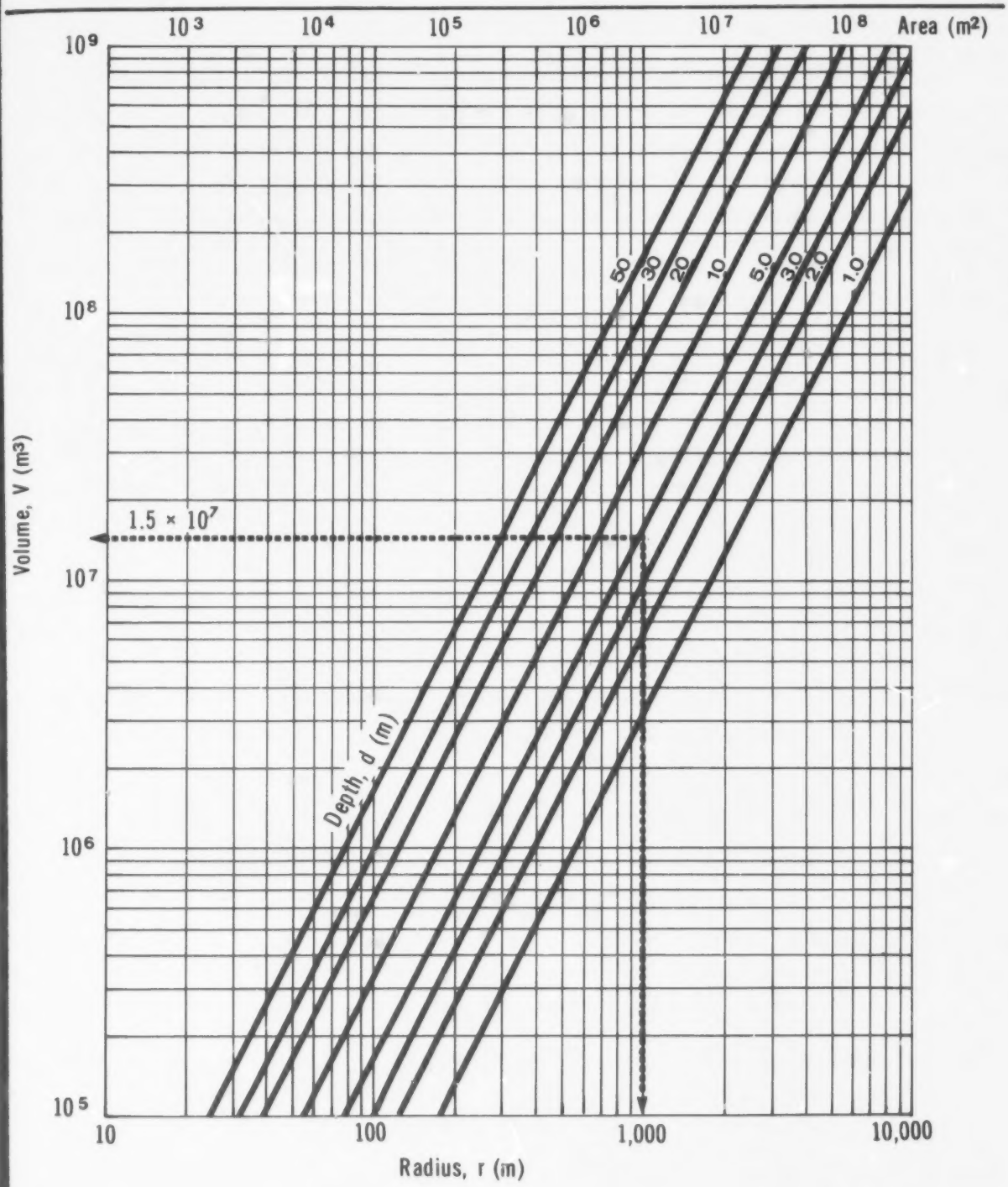


FIGURE 24

SULPHURIC ACID

## VOLUME vs RADIUS



in the cylinder can be obtained from Figure 24. The radius (r) represents the distance from the spill to the point of interest.

**Figure 25: Average concentration versus volume.** For a known volume of water (within the idealized cylinder of radius (r) and length (d)), the average concentration of pollutant (C) can be obtained from Figure 25 for a known mass of spill. This assumes the pollutant is spread evenly throughout the cylinder. For pollutants that are more or less dense than water, the actual concentration at the bottom would be higher or lower, respectively.

### 5.4.3 Sample Calculations.

**5.4.3.1 Pollutant concentration in non-tidal rivers.** A 20 tonne spill of 50 percent sulphuric acid solution has occurred in a river. The stream width is 50 m and the stream depth is 5 m. The average stream velocity is estimated at 1 m/s. What is the maximum concentration expected at a water intake located 5 km downstream?

Solution

Step 1: Define parameters

- W = 50 m
- d = 5 m
- U = 1 m/s
- mass = 20 tonnes of 50 percent solution, equivalent to 10 tonnes of 100 percent sulphuric acid
- X = 5,000 m

Step 2: Calculate time to reach point of interest

- Use Figure 18
- With X = 5,000 m and U = 1 m/s, t = 83 min

Step 3: Calculate hydraulic radius (r)

- Use Figure 19
- With W = 50 m and d = 5 m, r = 4.2 m

Step 4: Calculate longitudinal diffusion coefficient (E)

- Use Figure 20
- With r = 4.2 m and U = 1 m/s, E = 69 $m^2/s$

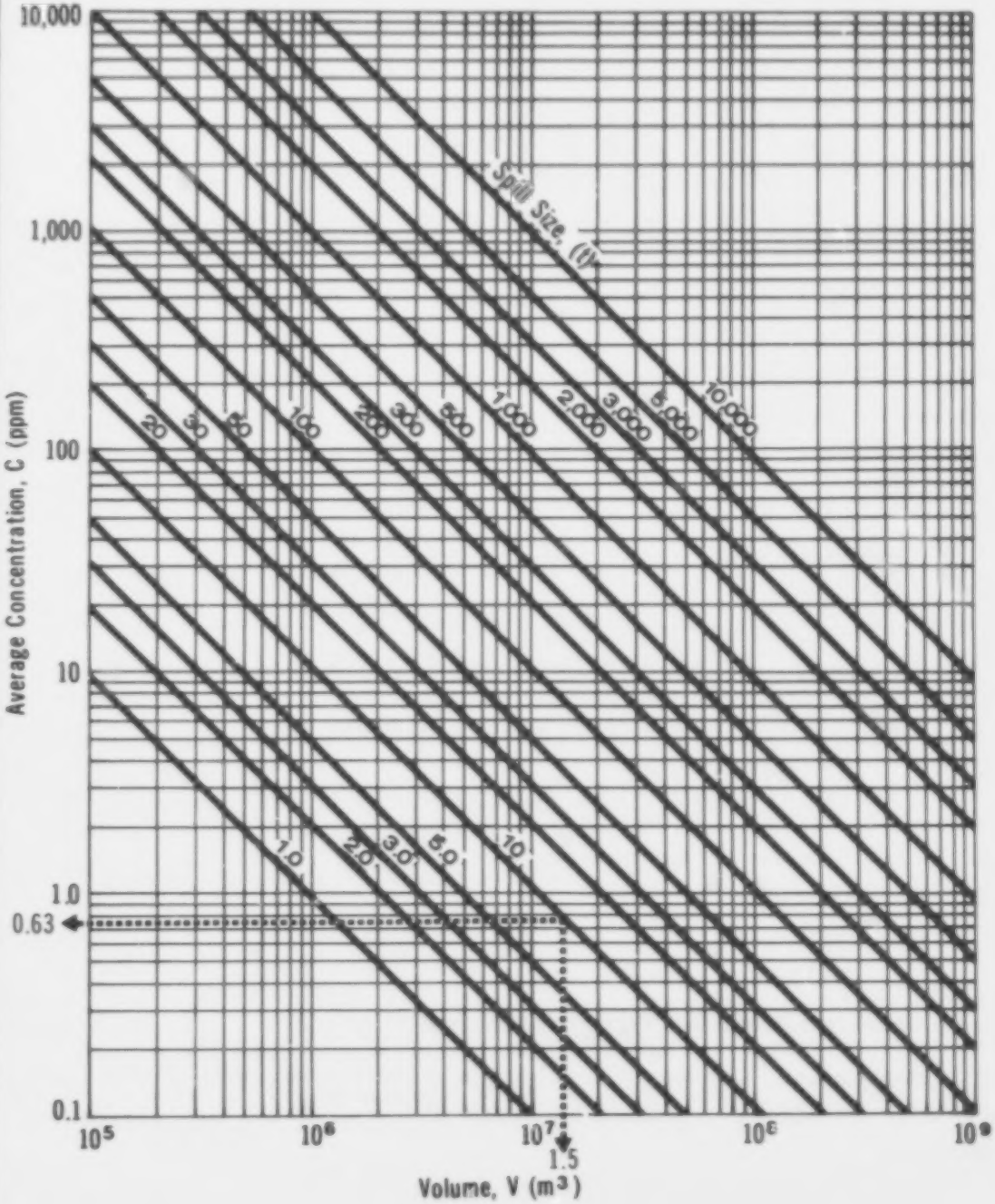
Step 5: Calculate alpha ($\alpha$)

- Use Figure 21
- With E = 69 $m^2/s$ and t = 83 min, $\alpha$ = 2,000

FIGURE 25

SULPHURIC ACID

## AVERAGE CONCENTRATION vs VOLUME



Step 6: Calculate delta ($\Delta$)

- Use Figure 22
- With alpha ($\alpha$) = 2,000 and mass = 10 tonnes, delta ($\Delta$) = 5

Step 7: Compute stream cross-sectional area (A)

- $A = W \times d = 50 \times 5 = 250\ m^2$

Step 8: Calculate maximum concentration (C) at point of interest

- Use Figure 23
- With $\Delta = 5$ and $A = 250\ m^2$, C = 20 ppm

**5.4.3.2 Average pollutant concentration in lakes or still water bodies.** A 20 tonne spill of 50 percent sulphuric acid solution has occurred in a lake. The point of interest is located on the shore approximately 1,000 m from the spill. The average depth between the spill site and the point of interest is 5 m. What is the average concentration which could be expected?

Solution

Step 1: Define parameters

- d = 5 m
- r = 1,000 m
- mass = 10 tonnes (equivalent 100 percent sulphuric acid)

Step 2: Determine the volume of water available for dilution

- Use Figure 24
- With r = 1,000 m, d = 5 m, the volume is approximately $1.6 \times 10^7\ m^3$

Step 3: Determine the average concentration

- Use Figure 25
- With $V = 1.6 \times 10^7\ m^3$ and mass = 10 tonnes, the average concentration is 0.63 ppm

## 5.5 Subsurface Behaviour: Penetration into Soil

**5.5.1 Mechanisms.** Concentrated sulphuric acid has a boiling point of 310°C at a pressure of 1 atmosphere. Consequently, when it is spilled onto soil only limited evaporation will occur below this temperature.

Since sulphuric acid is miscible with water, the presence of water in the soil or falling as precipitation at the time of the spill will influence the rate of chemical

movement in the soil. Concentrated sulphuric acid reacts violently with water producing much heat. Dilution through mixture with water will decrease the viscosity more than the mass density. This will have the net effect of increasing the velocity of downward movement in the soil.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or remain ponded.

For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement and thus represents a typical case.

During transport through the soil, sulphuric acid can dissolve some of the soil material, in particular carbonate-based materials. The acid will be neutralized to some degree. However, significant amounts of acid are expected to remain for transport down toward the groundwater table. The analysis used here neglects these retarding factors.

Upon reaching the groundwater table, the acid will continue to move in the direction of groundwater flow and downward since its mass density exceeds that of water. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the acid concentration somewhat. This is shown schematically in Figure 26.

**5.5.2 Equations Describing Sulphuric Acid Movement into Soil.** The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

**5.5.3 Saturated Hydraulic Conductivity of Sulphuric Acid in Soil.** The saturated hydraulic conductivity ($K_o$), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where:

$k$ = intrinsic permeability of the soil ($m^2$)

$\rho$ = mass density of the fluid ($kg/m^3$)

$\mu$ = absolute viscosity of the fluid (Pa•s)

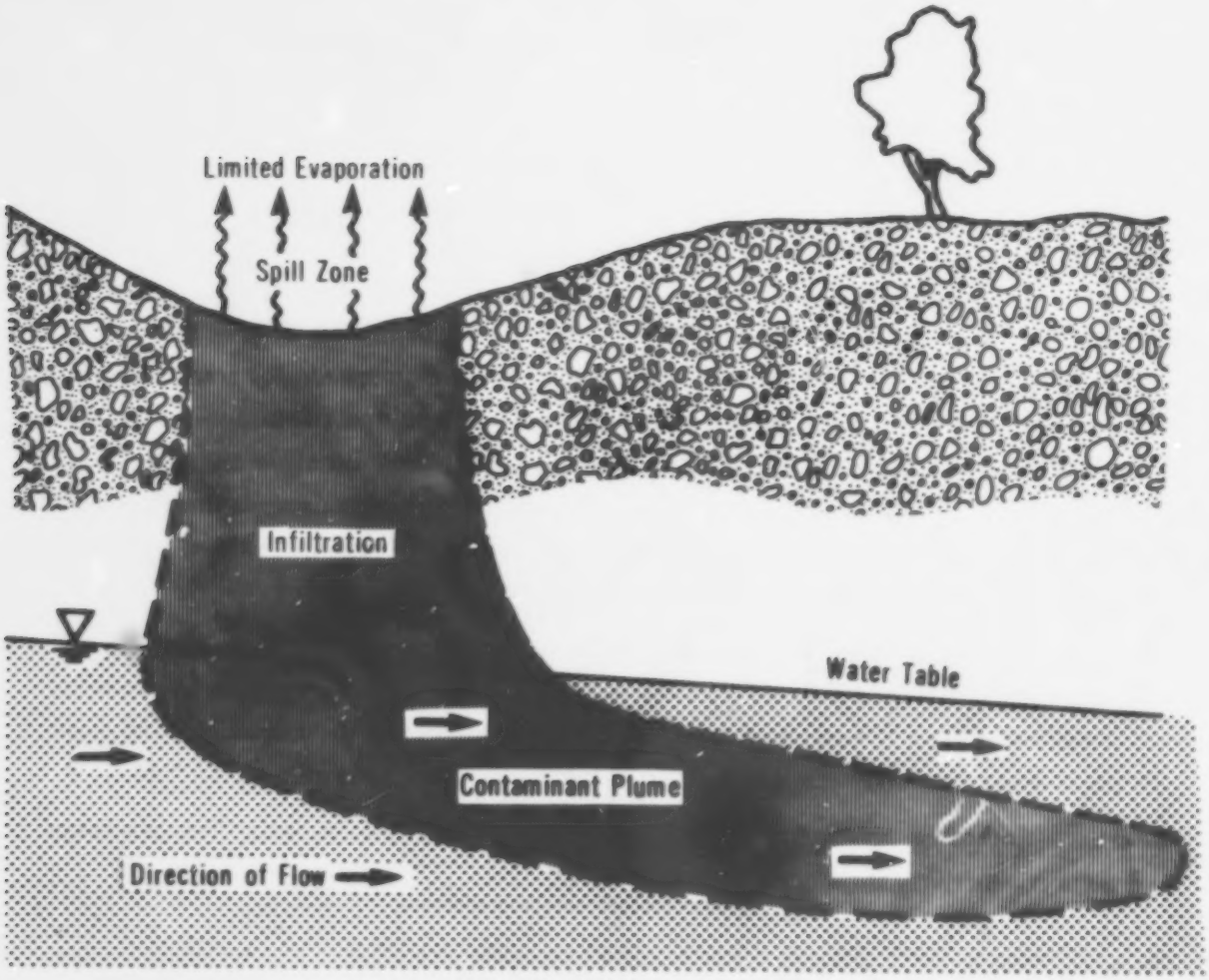
$g$ = acceleration due to gravity = 9.81 $m/s^2$

The fluids involved are sulphuric acid (60% by weight and concentrated) and water. The water calculations represent the extreme as sulphuric acid is diluted.

FIGURE 26

SULPHURIC ACID

## SCHEMATIC SOIL TRANSPORT




Soil: Coarse Sand

- Porosity (n) = 0.35
- Intrinsic Permeability (k) = $10^{-9}$ $m^2$
- Field Capacity ($\theta_{fc}$) = 0.075

| Property | Sulphuric Acid | | | Water |
|---|---|---|---|---|
| | Concentrated | 60% by Weight | | |
| | 20°C | 20°C | 4°C | 20°C |
| Mass density ($\rho$), kg/m$^3$ | 1,830 | 1,500 | 1,510 | 1,000 |
| Absolute viscosity ($\mu$), Pa•s | 25.4 x 10$^{-3}$ | 6.4 x 10$^{-3}$ | 8.8 x 10$^{-3}$ | 1.0 x 10$^{-3}$ |
| Saturated hydraulic conductivity ($K_o$), m/s | (0.07x10$^7$)k | (0.23x10$^7$)k | (0.17x10$^7$)k | (0.98x10$^7$)k |

5.5.4 **Soils.** The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

| Property | Soil Type | | |
|---|---|---|---|
| | Coarse Sand | Silty Sand | Clay Till |
| Porosity (n), m$^3$/m$^3$ | 0.35 | 0.45 | 0.55 |
| Intrinsic permeability (k), m$^2$ | 10$^{-9}$ | 10$^{-12}$ | 10$^{-15}$ |
| Field capacity ($\theta_{fc}$), m$^3$/m$^3$ | 0.075 | 0.3 | 0.45 |

5.5.5 **Penetration Nomograms.** Nomograms for the penetration of sulphuric acid into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time ($t_p$) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth, in time $t_p$.

A flowchart for the use of the nomograms is presented in Figure 27. The nomograms are presented in Figures 28, 29 and 30. The water line on the nomograms represents the maximum penetration of water at 20°C, in time $t_p$. It is a limiting condition as sulphuric acid becomes highly diluted with water.

FIGURE 27

SULPHURIC ACID

## FLOWCHART FOR NOMOGRAM USE

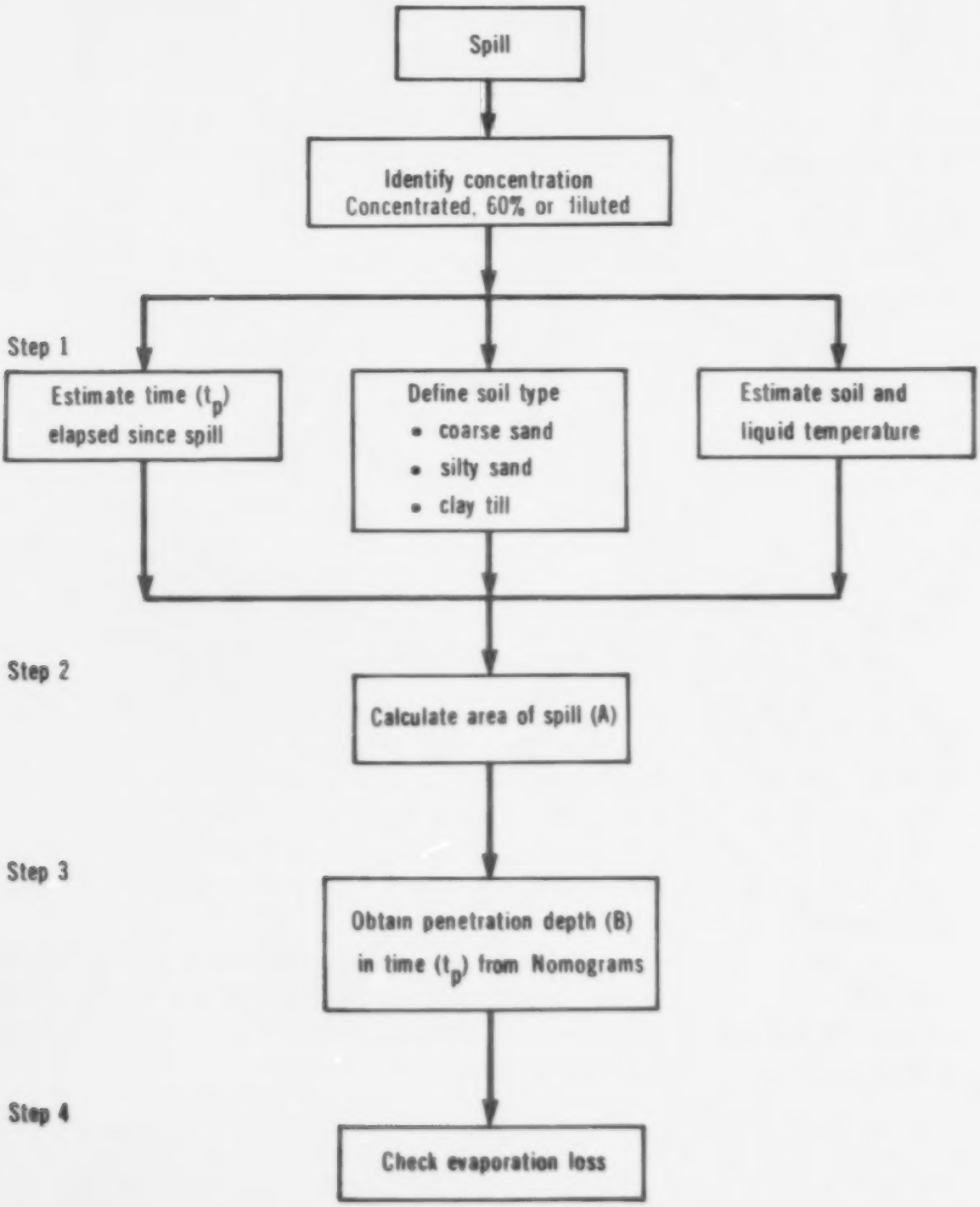


FIGURE 28

SULPHURIC ACID

## PENETRATION IN COARSE SAND

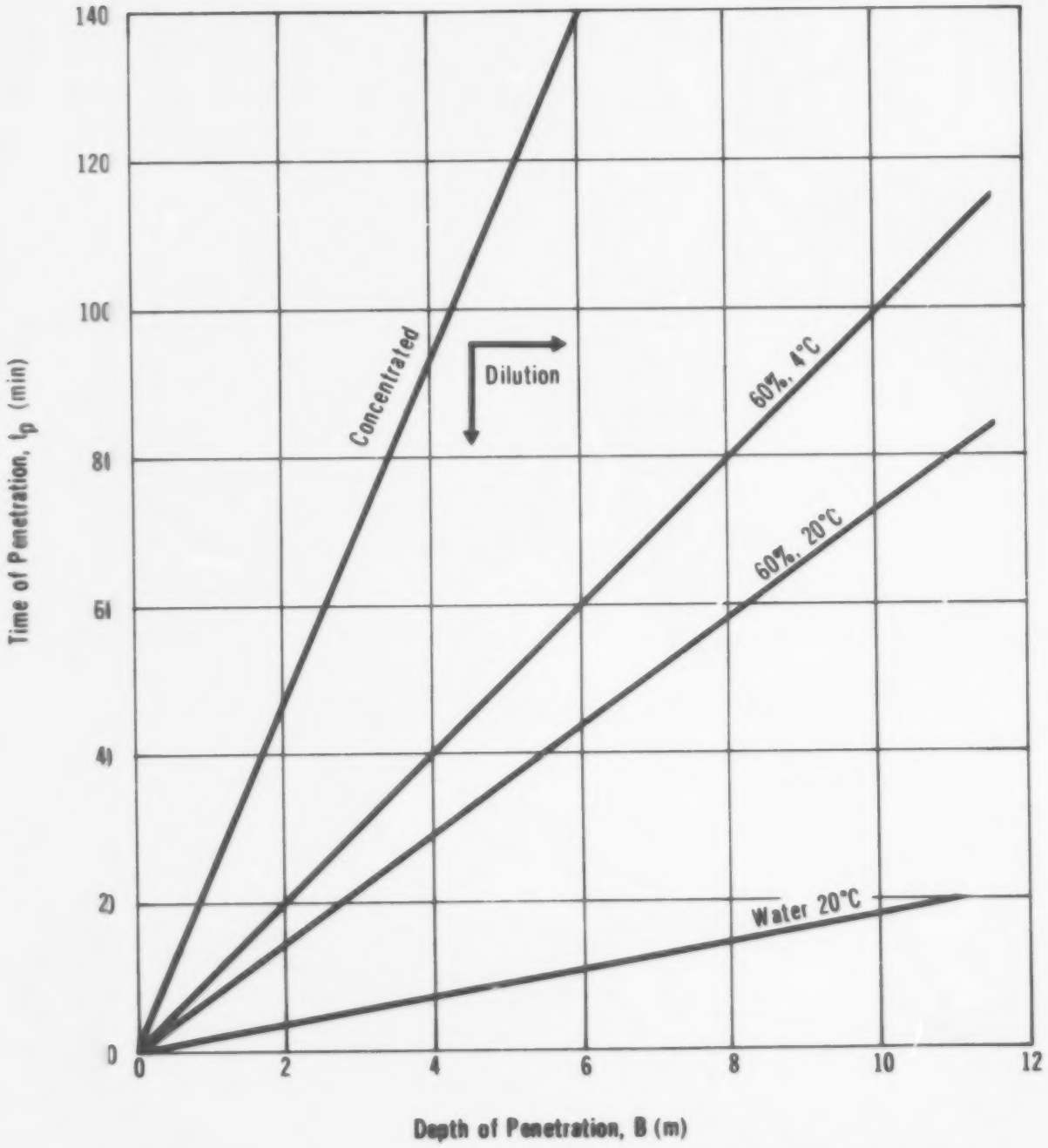


FIGURE 29

SULPHURIC ACID

## PENETRATION IN SILTY SAND

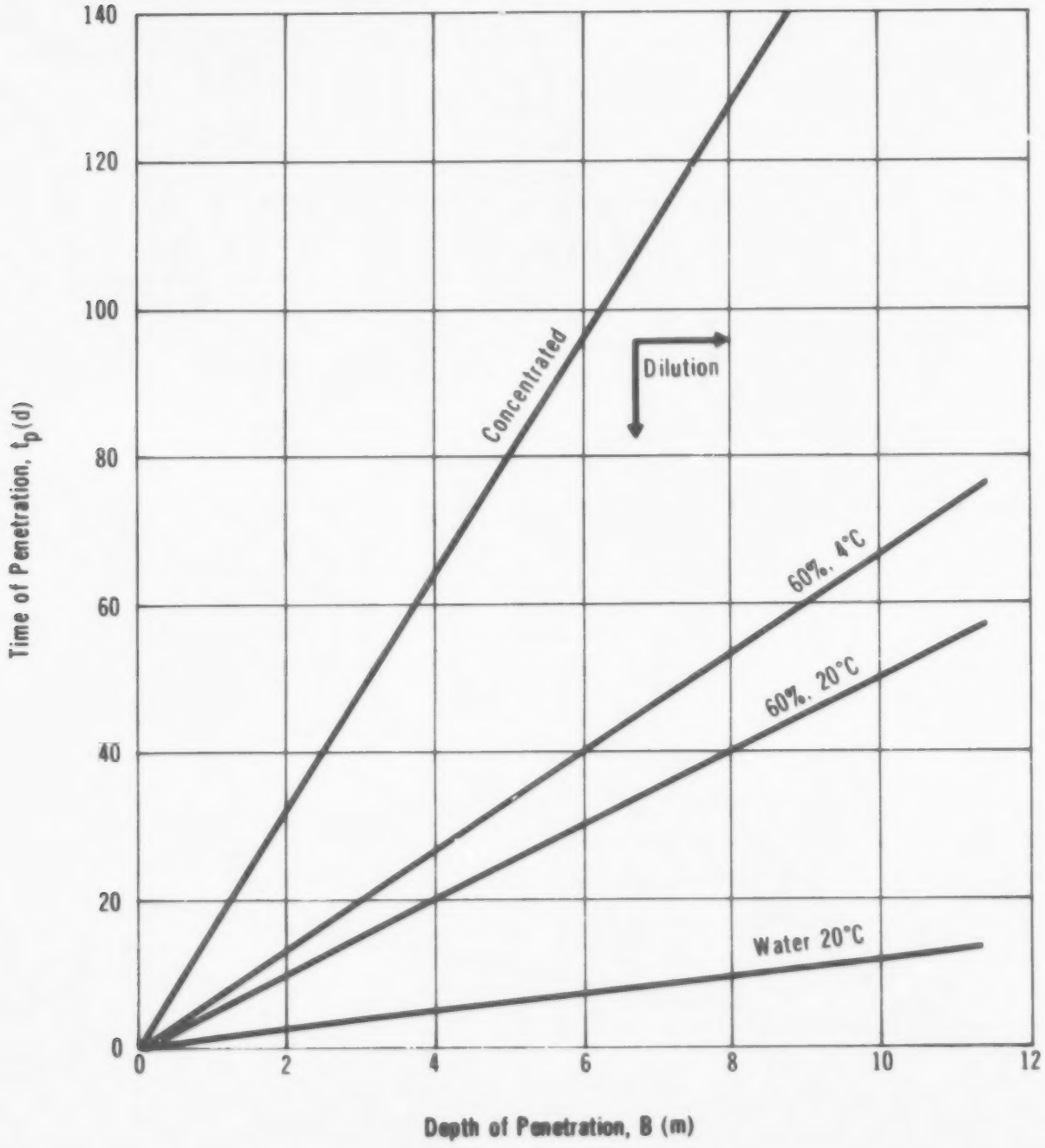
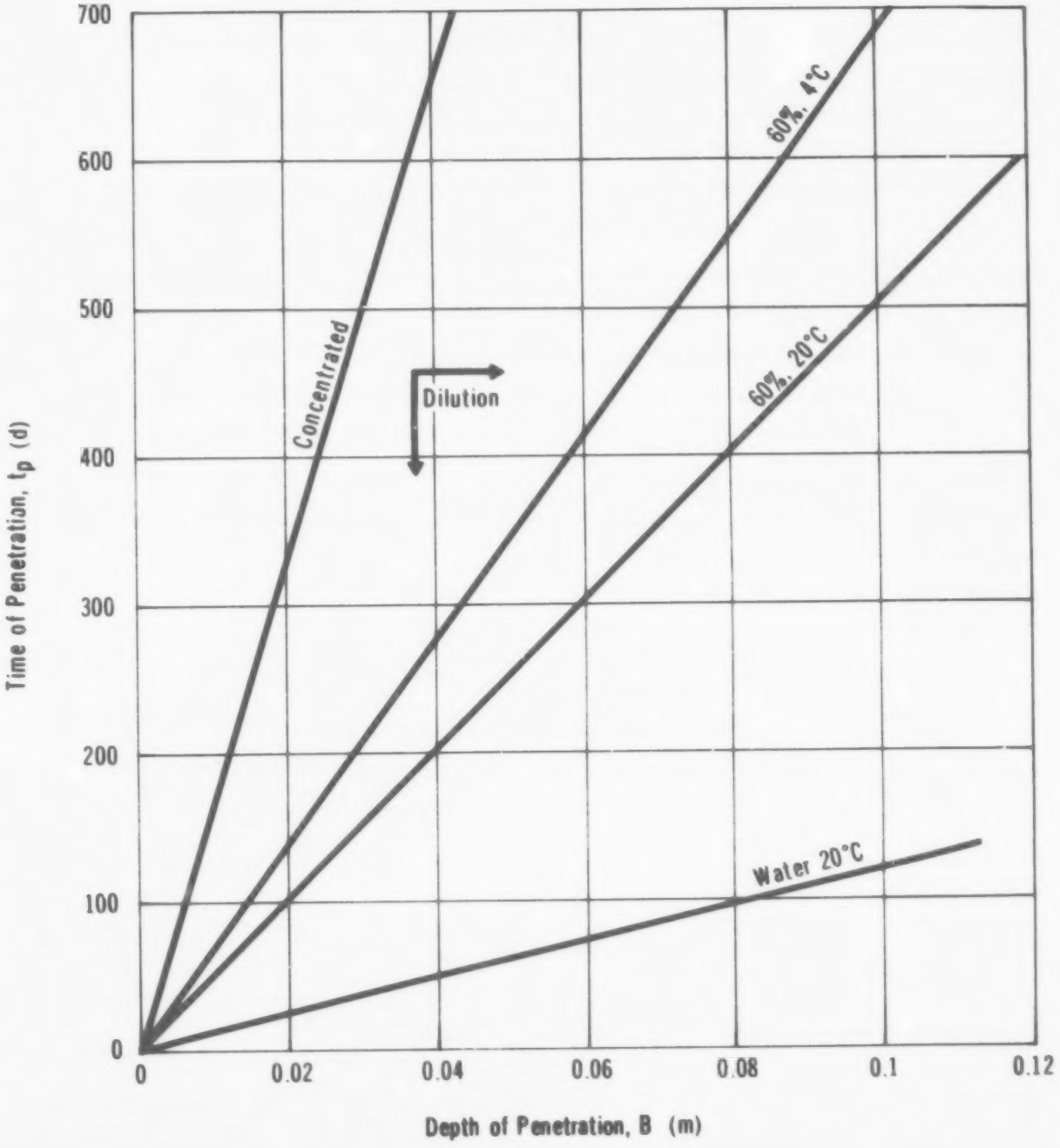


FIGURE 30

SULPHURIC ACID

## PENETRATION IN CLAY TILL



**5.5.6 Sample Calculation.** A 20 tonne spill of 60 percent sulphuric acid has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. Calculate the depth of penetration 40 minutes after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 20,000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill ($t_p$) = 40 min

Step 2: Calculate area of spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate depth of penetration (B) at time ($t_p$)

- For coarse sand, B = 5.5 m at $t_p$ = 40 min
- Groundwater table has not been reached in this time

Step 4: Check evaporation loss

- Evaporation of 60% sulphuric acid is negligible after 40 minutes under the spill conditions

# 6 ENVIRONMENTAL DATA

## 6.1 Suggested or Regulated Limits

### 6.1.1 Water.

**6.1.1.1 Canada.** Sulphuric acid in itself is not regulated in Canada; however, there are guidelines for both sulphate and pH.

Nationally, 500 mg/L sulphate is the recommended upper limit; 150 mg/L is preferred. For livestock, a limit of 1,000 mg/L sulphate is acceptable (WQS 1979).

Ontario recommends that "alkalinity should not be decreased by more than 25 percent of the natural concentration". The pH should not go below 6.5 (Water Management Goals 1978).

**6.1.1.2 Others.** In the United States, 250 mg/L sulphate is the maximum acceptable, with a 50 mg/L objective (WQCDB-2 1971); 500 mg/L is acceptable for livestock (EPA-440/9-75-009). The World Health Organization recommended a limit of 250 mg/L sulphate in 1961 (WQCDB-2 1971).

For high levels of protection from acidity, a pH of not less than 6.5 is recommended; pH 5.5 affords the minimum acceptable protection. The extreme range of pH fluctuation should not exceed 2.0 units; total alkalinity should not be reduced by more than 25 percent (WQC 1972).

**6.1.2 Air.** Ontario limits airborne sulphuric acid to 100 $\mu g/m^3$ (Ontario E.P. Act 1971).

## 6.2 Aquatic Toxicity

**6.2.1 U.S. Toxicity Rating.** Sulphuric acid and oleum have been assigned a $TL_m96$ (4-day median lethal toxicity rating) of 10 to 100 mg/L (RTECS 1979).

**6.2.2 Freshwater Toxicity.**

| Conc. (mg/L) | Time (hours) | Species | Result | Water Conditions | Reference |
|---|---|---|---|---|---|
| Fish Kill Data | | | | | |
| 6.0 - 8.0 | 6 | Minnows | harmful or lethal | 20°C, distilled | WQC 1963 |

| Conc. (mg/L) | Time (hours) | Species | Result | Water Conditions | Reference |
|---|---|---|---|---|---|
| 110 - 120 | 6 | Minnows | harmful or lethal | 20°C, hard | WQC 1963 |
| 7.36 | 60 | Bluegill | harmful or lethal | distilled | WQC 1963 |
| 6.25 | 24 | Trout | harmful or lethal | | WQC 1963 |
| Fish Toxicity Tests | | | | | |
| 42 | 48 | Mosquito fish | $TL_m$ | turbid | WQC 1963 |
| 49 | 48 | Bluegill | $TL_m$ | tap, 20°C | WQC 1963 |
| Microorganisms | | | | | |
| 0.1 | 168 | *Daphnia magna* | lethal | static-soft | Ellis 1967 |
| 88 | 64 | *Daphnia magna* | lethal | Lake Erie | WQC 1963 |
| Invertebrates | | | | | |
| 33.1 | not stated | Bivalve larvae | harmful | | WQC 1963 |

**6.2.3 Saltwater Toxicity.**

| Conc. (mg/L) | Time (hours) | Species | Result | Water Conditions | Reference |
|---|---|---|---|---|---|
| Fish Toxicity Tests | | | | | |
| 100 to 330 | 48 | Flounder | $LC_{50}$ | aerated | Portman 1970 |
| Invertebrates | | | | | |
| 100 | 120 | Oysters | 18% lethal | | WQC 1963 |
| 80 to 90 | 48 | Shrimp | $LC_{50}$ | aerated | Portman 1970 |

## 6.3 Toxicity to Other Biota

### 6.3.1 Livestock.

| Conc. (mg/L) | Species | Result | Water Conditions | Reference |
|---|---|---|---|---|
| 2,104 to 3,500 | Cattle | weakened and died | Minnesota drinking water - sulphate ion | WQCDB-2 1971 |

### 6.3.2 Plant.

| Conc. | Species | Result | Reference |
|---|---|---|---|
| Trees | | | |
| 10-2N (approx. pH 2.0) | Pears | caused black spots on fruit | Ebara 1980 |

| Conc. | Time (hours) | Species | Result | Reference |
|---|---|---|---|---|
| Crops | | | | |
| pH 1.0 and 2.0 (mist) | 48 | Corn | damage | Wedding 1981 |
| pH 0.5 (mist) | not stated | Corn | immediate damage | Wedding 1981 |
| 10% acid (mist) | not stated | Soybean (4 to 6 wk old) | severe necrotic lesions on leaves | Wedding 1979 |
| 18 M (mist) | 10 h/d for 14 d | Soybean (4 to 6 wk old) | no visible toxicity damage | Wedding 1979 |
| 100 to 200 $mg/m^3$ | 4 to 16 | Plants | marginal and tip necrosis of foliage | Lang 1979 |

**6.3.2.1 Plant studies.** Different plant species vary greatly in sensitivity to sulphuric acid aerosol; injury to sensitive species appears to be conditioned by biological as well as physiological factors (Lang 1979).

## 6.4 Other Air and Land Toxicity

Atmospheric aerosols contain varying quantities of both weak and strong acids. Measurements have demonstrated that strong acid concentrations equivalent to approximately 20 $\mu g/m^3$ of sulphuric acid may exist in the ambient atmosphere for periods of several hours. Strong acid may frequently be present in low amounts in "fine" aerosol particles (Tanner 1981).

## 6.5 Effect Studies

The poisonous effect of sulphuric acid is primarily due to its acidity. While a pH of 4.0 has caused gill irritation, pH 3.5 has caused death in sunfish, bass and carp. As a consequence of this pH effect, a quantity of acid that would be lethal in soft water could be rendered harmless in hard or highly buffered water.

Generally, a pH greater than 4.5 permits fish to survive; other aquatic life requires at least a pH of 5.5. Below pH 5, specialized aquatic flora and fauna develop (WQC 1963).

Summary of pH effects (WQC 1972):

| | |
|---|---|
| 5.5-6.0 | Eastern brook trout survive.<br>Rainbow trout do not occur.<br>Growth rate of carp is reduced.<br>Spawning is reduced.<br>Molluscs are rare. |
| 5.0-5.5 | Smaller populations of fish, but not lethal.<br>May be lethal to eggs or larvae and some invertebrates. Algae and higher plants will grow. |
| 4.5-5.0 | No viable fishery can be maintained.<br>Likely to be lethal to eggs and fry.<br>Harmful to carp. Lethal to some invertebrates. |
| 4.0-4.5 | Only a few fish species survive.<br>Only pike reproduce. |
| 3.5-4.0 | All flora and fauna are severely restricted. |
| 3.0-3.5 | Unlikely that any fish survive more than a few hours. |

**6.6 Degradation**

Sulphuric acid does not chemically or biologically degrade naturally; however, it is neutralized and/or converted with time.

**6.7 Long-term Fate and Effect**

Sulphuric acid will ultimately react with calcium and magnesium in water to form sulphate salts. There is no bioaccumulation or food chain concentration effect cited.

**6.8 Soil**

**6.8.1 Soil Degradation of Material.**

| Conc. (kg/ha/yr) | Time | Species | Effect | Reference |
|---|---|---|---|---|
| 25 to 50 | 2 wk intervals | Conifer forest soils | little or no effect on cation removal or nitrification in soil; 15% increase in fresh needle decomposition | Roberts 1980 |

**6.8.2 Effect of Soil Chemistry.** Sulphuric acid has led to increased weathering of calcium from soils and rocks so that the calcium ion rises in concentration in waters above pH 6, and also in those below pH 5 (NRCC 1977).

**6.9 Other Effects**

**6.9.1 Possible Effects on Water Treatment Process.** Sulphuric acid interferes with some normal biological processes: 58 mg/L has caused 50 percent inhibition of sewage organisms (DPIMR 1981).

# 7 HUMAN HEALTH

The immediate and obvious effects of concentrated sulphuric acid splashes on living tissue may account for the limited amount of published report material dealing with skin contact, exposure, and ingestion. There are, however, numerous literature reports noting the animal and human health effects of inhalation of sulphuric acid mist and fuming sulphuric acid ($SO_3$). Scant literature was encountered on the effects of sulphuric acid exposure on reproduction and mutagenicity. There was no literature reporting on carcinogenicity. Testing to determine potential teratogenicity of sulphuric acid has yielded largely negative results. That sulphuric acid continues to be a topic of current interest is reflected in the 14 studies reported in TOX TIPS (a summary of current research activity) since 1976; all but one study examined inhalation toxicity.

Sulphuric acid was reported in the 1980 EPA TSCA inventory (RTECS (on-line) 1981). Published work on sulphuric acid has been reviewed recently. The data summarized here are representative of information in the literature.

The toxicological data summarized here have been extracted from reliable standard references only. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations. Only acute (short-term) exposure data are given for non-human mammalian species, to support interpretation of the human data where appropriate.

## 7.1 Recommended Exposure Limits

The exposure standards for sulphuric acid are based upon its irritant properties. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

| Guideline (Time) | Origin | Recommended Level | Reference |
|---|---|---|---|
| Time-weighted Averages (TWA) | | | |
| TLV* (8 h) | USA-ACGIH | 1.0 mg/m$^3$ | TLV 1981 |
| PEL (10 h) | NIOSH | 1.0 mg/m$^3$ | NIOSH Guide 1978 |
| Not stated | USSR | 1.0 mg/m$^3$ | NIOSH 1981 |
| Not stated | Romania | 0.5 mg/m$^3$ | NIOSH 1981 |
| Short-term Exposure Limits (STEL) | | | |
| STIL* (5 min) | - | 10 mg/m$^3$ | CHRIS 1978 |

| Guideline (Time) | Origin | Recommended Level | Reference |
|---|---|---|---|
| STIL* (10 min) | - | 5 mg/m$^3$ | CHRIS 1978 |
| (15 min) | Saskatchewan | 3 mg/m$^3$ | Sask. 1981 |
| STIL* (30 min) | - | 2 mg/m$^3$ | CHRIS 1978 |
| Ceiling | Romania | 1.5 mg/m$^3$ | NIOSH 1981 |
| STIL* (60 min) | - | 1 mg/m$^3$ | CHRIS 1978 |
| Other Human Toxicities | | | |
| IDLH | USA | 80 mg/m$^3$ | NIOSH Guide 1978 |
| $TC_{LO}$ (24 wk) | | 3 mg/m$^3$ | RTECS (on-line) 1981 |
| $TC_{LO}$ | | 800 µg/m$^3$ | AAR 1981 |
| $TC_{LO}$ (15 min) | | 5 mg/m$^3$ | AAR 1981 |
| $TC_{LO}$ | | 800 µg/m$^3$ | ITII 1981 |
| $TD_{LO}$ | | 135 mg/kg | RTECS (on-line) 1981 |

*STIL Short-term Inhalation Limit

**7.2 Irritation Data**

**7.2.1 Skin Contact.**

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| SPECIES: Human | | |
| Concentrated form | Rapid destruction of tissue, severe burns, necrosis | DPIMR 1981 |
| Unspecified | Cicatrization with disfigurement | Goldman et al. 1953. IN NIOSH 1974 |
| 77-98% Acid | Severe second and third degree burns | CHRIS 1978 |
| Dilute solutions | Repeated contact may cause dermatitis | Sax 1979 |

### 7.2.2 Eye Contact.

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| SPECIES: Human | | |
| Concentrated form | Extremely severe damage, often leading to blindness | NIOSH Guide 1978 |
| Unspecified | Irreparable corneal damage resulting in blindness | Fasullo 1965. IN NIOSH 1974 |
| Mist | Irritation | Amdur et al. 1953. IN NIOSH 1974 |
| Vapours from hot acid (77 to 98%) | Moderate irritation | CHRIS 1978 |
| SPECIES: Rabbit | | |
| 1,380 µg | Severe irritation | RTECS 1979 |

## 7.3 Threshold Perception Properties

### 7.3.1 Odour.

Odour Characteristics: Odourless unless heated, then choking (AAR 1981).

Odour Index: 5,368 at 146°C (AAR 1981).

| Parameter | Media | Concentration | Reference |
|---|---|---|---|
| 100% Detection | - | 3 $mg/m^3$ | Lippmann 1980 |
| Odour Threshold | air | >1 $mg/m^3$ | CHRIS 1978 |
| Threshold Odour Concentration | air | >1 $mg/m^3$ | AAR 1981 |
| Median Recognition Threshold | air | 0.6 $mg/m^3$ | AAR 1981 |
| Subjective Limit of Detection | - | 0.5 to 0.7 $mg/m^3$ | NIOSH 1974 |

### 7.3.2 Taste. Taste Characteristic: Sour

| Parameter | Media | Concentration | Reference |
|---|---|---|---|
| Detection Threshold | water | 0.0013 g/100 mL | ASTM 1980 |
| Detection Threshold | water | 0.001 normality | ASTM 1980 |

## 7.4 Long-term Studies

### 7.4.1 Inhalation. (Data for sulphuric acid mist unless otherwise specified.)

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| Acute Exposures | | |
| SPECIES: Human | | |
| 800 µg/m$^3$ | $TC_{LO}$ | AAR 1981 |
| 3 to 39 mg/m$^3$ (10 min to 1 h) 1.0 µm MMD | Pulmonary resistance was increased more than 20% in most subjects and in some cases was as high as 150% above control values. Transient cough and broncho-constriction were present | Lippmann 1980 |
| 3 to 39 mg/m$^3$ 10 N acid mist, 1 µm mean diameter; 11.5 to 38 mg/m$^3$ 4 N acid mist, 1.5 µm mean diameter (up to 60 min) | Irritant effect of 20.8 mg/m$^3$ at high humidity and larger particle size was greater than that of 39.4 mg/m$^3$ at lower humidity and smaller particle size. Increase in airway resistance was higher in the high humidity exposed group | Sim and Pattle 1957. IN NIOSH 1974 |
| 12 mg/m$^3$ and 0.6 mg/m$^3$ | Significant concentrations of ammonia gas in respiratory tract may protect against low levels of acid aerosols and vapours | Larson et al. 1977. IN NIOSH 1981 |
| 8.3 to 3.12 mg/m$^3$ (expressed as $SO_2$) | Author experienced nosebleeds | Dorsch 1913. IN NIOSH 1974 |
| 6.0 to 2.4 mg/m$^3$ | Acute irritation of mucous membranes. Reflexive cough. Eye irritation | Bushtueva 1957. IN NIOSH 1974 |
| 5 mg/m$^3$ (15 min) | $TC_{LO}$, toxic pulmonary effects | ITII 1981 |
| 5 mg/m$^3$ (15 min) | $TC_{LO}$ | AAR 1981 |
| 5 mg/m$^3$ (5 to 15 min) | Deep breath produced coughing | Doc. TLV 1981 |
| 5 mg/m$^3$ | Cough, increase in respiratory rate, and impairment of ventilatory capacity | NIOSH/OSHA 1981 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 5 to 0.4 mg/m$^3$ (5 to 15 min) 1 µm particle size | Increase in respiratory rate, decrease in tidal volume. These changes occurred within 2 minutes of commencing inhalation | Amdur et al. IN Lippmann 1980 |
| 5 to 0.4 mg/m$^3$ (5 to 15 min) 1 µm particle size) | Retention of sulphuric acid in the respiratory tract averaged 77% over a 0.4 to 1.0 mg/m$^3$ exposure concentration range | Admur et al. 1952 IN NIOSH 1974 |
| 2.4 to 1.1 mg/m$^3$ | Irritation at the base of esophagus. Some subjects noted eye irritation | Bushtueva 1957. IN NIOSH 1974 |
| 2.0 to 1.8 mg/m$^3$ | Increase in respiratory rate | Bushtueva 1957. IN NIOSH 1974 |
| >1,000 µg/m$^3$ | Mild reversible broncho-constriction | Liekauf 1981 |
| 1,000 µg/m$^3$ (16 min) | Small but statistically significant changes in specific conductance | Liekauf 1981 |
| 1 mg/m$^3$ (1 h) | Administered by nasal mask, mean bronchial clearance half-time was increased by 48% | Lippmann 1980 |
| 1 mg/m$^3$ 0.5 mm MMD | Speeding in mucociliary clearance time probably due to irritant response | Newhouse et al. 1978. IN NIOSH 1981 |
| 1,000 to 10 µg/m$^3$ (10 min) | No significant alteration of lung volumes, distribution of ventilation, ear oximetry, dynamic mechanics of breathing, oscillation mechanics of chest-lung system, pulmonary capillary blood flow, diffusing capacity, oxygen consumption. pulmonary tissue volume | Sackner et al. 1978. IN NIOSH 1981 |
| 980 µg/m$^3$ (1 h) | Significant transient slowing of tracheobronchial mucociliary clearance | Liekauf 1981 |
| 0.85 to 0.6 mg/m$^3$ | Detection of throat tickling and scratching | Bushtueva 1957. IN NIOSH 1974 |
| 800 µg/m$^3$ | $TC_{LO}$, toxic mouth effects | ITII 1981 |
| 0.73 mg/m$^3$ | 19% prolongation of optical chronaxy (1 subject) | Bushtueva 1961. IN NIOSH 1974 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 0.7 mg/m$^3$ | 24% increase in sensitivity to light (3 subjects) | Bushtueva 1961. IN NIOSH 1974 |
| 0.7 and 0.3 mg/m$^3$ | No potentiation effect between sulphuric acid aerosol and sulphur dioxide at 0.65 and 3 mg/m$^3$ to light sensitivity in 3 women | Bushtueva 1961. IN NIOSH 1974 |
| 0.5, 0.4, 0.35 mg/m$^3$ (5 to 15 min) 1.0 µm mean particle size | Increased respiratory rate | Amdur et al. 1952. IN NIOSH 1974 |
| 110µg/m$^3$ (1 h) | Significant acceleration in mucociliary clearance. Group mean tracheobronchial clearance half-time, TB1/2, decreased from 80 to 50 minutes | Liekauf 1981 |
| 0.1 mg/m$^3$ (1 h) | Administered by nasal mask, mean bronchial clearance half-time reduced by 38% | Lippmann 1980 |
| 100 µg/m$^3$ (2 h, 2 or 3 consecutive d) 0.5 or 0.59 µm MMD | No significant adverse changes in pulmonary function, including FVC, FEV, maximum expiratory flows with 50% and 25% of FVC remaining to be expired, total lung capacity, residual volume or total respiratory resistance | Avol et al. 1979. IN NIOSH 1981 |
| 100 µg/m$^3$ (4 h) 0.5 µm MMD | No significant difference between control and aerosol exposed group for glutathione, lysozyme, glutathione reductase, serum glutamic oxaloacetic transaminase, serum vitamin E, and 2,3-diphosphoglyceric acid | Chaney et al. 1980. IN NIOSH 1981 |
| 10 to 20 ppm | Unbearable | DPIMR 1981 |
| 1.5 to 2.5 ppm | Definitely unpleasant | DPIMR 1981 |
| 0.125 to 0.5 ppm | Mildly annoying | DPIMR 1981 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| SPECIES: Donkey | | |
| 1,000 to 200 $\mu g/m^3$ (1 h) 0.5 $\mu m$ mist | 3 out of 4 animals demonstrated short-term slowing of bronchial mucociliary clearance. 2 of 4 animals showed a more persistent slowing of clearance values after about 6 exposures | Lippmann 1980 |
| SPECIES: Guinea Pig | | |
| 200 $mg/m^3$ (1 h) | $LC_{50}$ | RMLTHH 1972 |
| 109 $mg/m^3$ (8 h) 0.4 $\mu m$ MMAD | $LC_{50}$. Hyperinflated lungs | Wolff et al. 1979. IN NIOSH 1981 |
| 60 to 20 $mg/m^3$ (8 h) | $LC_{50}$. Death results from severe laryngeal spasm and bronchoconstriction. At concentrations which are lethal, 2.7 $\mu m$ particles are more toxic than 0.8 $\mu m$ particles | Doc. TLV 1981 |
| 50 $mg/m^3$ (8 h) 1 $\mu m$ particle size | $LC_{50}$, adult guinea pigs | NIOSH/OSHA 1981 |
| 40 to 2 $mg/m^3$ 0.8, 2.5 and 7 $\mu m$ MMD | Largest particles, 7 $\mu m$ at 30 $mg/m^3$, produced only slight increase in airway resistance. 0.8 $\mu m$ particles produced significant increase in resistance at 1.9 $mg/m^3$. At 40 $mg/m^3$, the 2.5 $\mu m$ particles produced greatest increase in resistance. Large particles probably act to produce mucosal swelling, exudation of fluid; smaller particles produce simple reflex bronchoconstriction | Amdur 1958. IN NIOSH 1974 |
| 30 $mg/m^3$ (8 h) 0.8 $\mu m$ MMAD | $LC_{50}$. Hemorrhage and transudation | Wolff et al. 1979. IN NIOSH 1981 |
| 30 $mg/m^3$ (1 h) 7 $\mu m$ particle size | 50% increase in pulmonary flow resistance. Particles of this size penetrate only to the upper respiratory tract and nasal passages | Doc. TLV 1981 |
| 18 $mg/m^3$ | $LC_{50}$ | RTECS 1979 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 18 mg/m$^3$ (8 h)<br>1 µm particle size | $LC_{50}$, young guinea pigs | NIOSH/OSHA 1981 |
| 8 mg/m$^3$ (8 h, 72 h)<br>1 µm particles | Some lung pathology at 8 hours. Increasing exposure time to 72 hours increased the severity of lung pathology | Doc. TLV 1981 |
| 6 mg/m$^3$ (1 h)<br>2.5 µm particle size | 50% increase in pulmonary flow resistance | Doc. TLV 1981 |
| 3 mg/m$^3$ (1 h)<br>1.8 µm CMD<br>0.32 mg/m$^3$ (1 h)<br>0.6 µm CMD<br>0.03 mg/m$^3$ (1 h)<br>0.25 µm CMD | Animals exposed to 3 mg/m$^3$ acid and Streptococcus showed 60% greater deposition rate of bacteria. Authors concluded sulphuric acid exposure can result in pathophysiologic effects as well as respiratory physiologic alterations | Fairchild et al. 1975 IN NIOSH 1981 |
| 2 mg/m$^3$ (5 d) | Pulmonary edema, thickening of alveolar walls | Bushtueva 1957. IN NIOSH 1974 |
| 1 or 0.51 or<br>0.1 mg/m$^3$ (1 h)<br>0.3 µm MMD; 0.69 or<br>0.4 or 0.11 mg/m$^3$<br>(1 h) 1 µm MMD | Dose-related increases in pulmonary flow resistance. Except for 0.11 mg/m$^3$ exposures, pulmonary flow resistance did not return to normal values by 30 minutes after exposure | Amdur et al. 1978. IN NIOSH 1981 |
| 0.7 mg/m$^3$ (1 h)<br>1 µm particle size | 50% increase in pulmonary flow resistance | Doc. TLV 1981 |
| 0.3 mg/m$^3$ (1 h)<br>0.3 µm particle size | 50% increase in pulmonary flow resistance | Doc. TLV 1981 |
| 48 ppm (1 h) | $LC_{LO}$ | RTECS 1979 |
| SPECIES: Mouse | | |
| 549 mg/m$^3$ (35 h) | $LC_{LO}$ | Treon et al. 1950. IN NIOSH 1974 |
| 500 mg/m$^3$ (8 h) | $LC_{50}$ | AAR 1981 |
| 165 mg/m$^3$ | $LC_{LO}$ | AAR 1981 |
| 140 ppm (3.5 h) | $LC_{LO}$ | RTECS 1979 |
| SPECIES: Rat | | |
| 347 ppm (1 h) | $LC_{50}$ | RTECS 1979 |
| 178 ppm (7 h) | $LC_{LO}$ | RTECS 1979 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 699 mg/m$^3$ | $LC_{LO}$ | Treon et al. 1950. IN NIOSH 1974 |
| 500 mg/m$^3$ | $LC_{LO}$ | AAR 1981 |
| SPECIES: Hamster | | |
| 1.1 mg/m$^3$, 1.5 mg/m$^3$ carbon black particles or carbon black particles onto which sulphuric acid has been condensed | Cytotoxic effects on tracheal tissue exposed to carbon/acid particles were greater than damage produced by either acid or carbon alone | Schiff et al. 1979. IN NIOSH 1981 |
| 1 mg/m$^3$ (2 h) 0.24 to 0.3 µm VMD | Depressed tracheal ciliary activity when exposed to sulphuric acid alone | Grose et al. 1980. IN NIOSH 1981 |
| Ozone 196 µg/m$^3$ (3 h) | In sequential exposure to ozone and then sulphuric acid, lowering of ciliary beating frequency was significantly less than with exposure to sulphuric acid alone | Grose et al. 1980. IN NIOSH 1981 |
| Chronic Exposures | | |
| SPECIES: Human | | |
| 35 to 12.6 mg/m$^3$ | Decrease in forced expiratory volume. Slightly greater acidity in salivary pH of exposed group. 40% of exposed workers had dental erosion, discolouration | El-Sadik 1972. IN NIOSH 1974 |
| 16 to 3 mg/m$^3$ | Severe erosion of teeth | Doc. TLV 1981 |
| 3 mg/m$^3$ (24 wk) | $TC_{LO}$, mouth effects | RTECS 1979 |
| 2.5 to 0.8 mg/m$^3$ | Less severe erosion of teeth | Doc. TLV 1981 |
| SPECIES: Monkey | | |
| 4.79 mg/m$^3$ (2 yr) | Moderate to severe histopathology | Doc. TLV 1981 |
| >2.5 mg/m$^3$ | Impaired pulmonary function | Alarie et al. 1971. IN NIOSH 1981 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 2.43 mg/m$^3$ (2 yr) 3.6 µm particle size | Moderate changes in histopathology, moderate alteration in distribution of ventilation, and a slight decrease in arterial $O_2$ | Doc. TLV 1981 |
| 0.48 mg/m$^3$ (2 yr) | Slight alteration in distribution of ventilation | Doc. TLV 1981 |
| 0.38 mg/m$^3$ (2 yr) 2.15 µm particle size | Slight histopathology | Doc. TLV 1981 |
| 0.1 to 1 mg/m$^3$ | Slight histopathologic changes in pulmonary tissues | Alarie et al. 1975. IN NIOSH 1981 |
| SPECIES: Guinea Pig | | |
| 25 mg/m$^3$ (2 d, 6 h/d) 1 µm MMD | Collapsed, fluid-filled areas of lung. Edema, hemorrhage. Macrophages in alveoli. Interstitial edema and vesiculation of capillary endothelium | Cockrell et al. 1978. IN NIOSH 1981 |
| 10 mg/m$^3$ and/or 0.5 ppm ozone (6 h/d, 5 d/wk for 2 mo) | Minimal proliferation of alveolar macrophages, mild tracheal changes. No evidence of a synergistic effect for combined exposure | Cockrell et al. 1978. IN NIOSH 1981 |
| 5 mg/m$^3$ (16 h/d, 7 d/wk, for 45 or 90 d) | Increase in total lung capacity after 90-day exposure. Ratio of functional residual capacity to total lung capacity lower at 45 days | Pepelko et al. 1979. IN NIOSH 1981 |
| 4 to 1 mg/m$^3$ (18 to 140 d) particle sizes at 0.6, 0.9 and 4 µm | The 0.9 µm particles produced greatest effects including slight lung edema, rare capillary hemorrhages | Thomas et al. IN NIOSH 1974 |
| 4 mg/m$^3$ (up to 140 d, 24 h/d) | Pulmonary pathology | Doc. TLV 1981 |
| 2 mg/m$^3$ (2 to 3 mo) | Slight catarrhal reaction in tracheal and bronchial mucosa with interstitial proliferation. Round lympoid cell infiltration around blood vessels and bronchi | Bushtueva 1957. IN NIOSH 1974 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| 0.10 mg/m$^3$ (up to 52 wk, at 23 h/d) 2.8 µm MMD 0.08 mg/m$^3$ (up to 52 wk, at 23 h/d) 0.8 µm MMD | Normal growth and survival rates, normal lung function test results. No exposure related changes in lungs, trachea, peribronchial lymph nodes, heart, liver, or kidneys | Best et al. 1966. IN NIOSH 1981 |
| SPECIES: Rat | | |
| 1.1 mg/m$^3$ and 0.5 ppm ozone (3 d, 14 d) | Increased tracheal glycoprotein secretion. Increased DNA, RNA content in lung homogenate | Last and Cross 1978. IN NIOSH 1981 |
| SPECIES: Mouse | | |
| 20 or 5 mg/m$^3$ (7 h/d during major period of organogenesis) | No teratogenicity noted | Murray et al. 1979. IN NIOSH 1981 |
| Carbon black particles onto which sulphuric acid vapour had been condensed: 1.4 ± 0.4 mg $H_2SO_4$/m$^3$ on carbon black particles: 1.5 ± 0.4 mg carbon/m$^3$ | Alterations of defense system suggest prolonged exposure to low concentrations of sulphuric acid and carbon particle mixtures reduces ability of mice to resist secondary stress of respiratory infection | Fenters et al. 1979. IN NIOSH 1981 |

**7.4.2 Ingestion.** (Data for sulphuric acid solutions.)

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| SPECIES: Human | | |
| Accidental ingestion 50% w/v | Damage from lips to colon. Most severe in pylorus and antrum. Severe stomatitis, strictures of esophagus, gastroesophageal junction and gastric antrum. Coagulation necrosis of the stomach, duo- | Jelenko et al. 1974. IN NIOSH 1981 |

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| | denum, jejunum and ileum. Pancreatitis. Omental fat necrosis. Severe peritonitis. Surgical intervention necessary | |
| SPECIES: Rat | | |
| 2,140 mg/kg | $LD_{50}$ | RTECS 1979 |

**7.4.3 Teratogenicity.**

| Exposure Level (and Duration) | Effects | Reference |
|---|---|---|
| SPECIES: Rabbit | | |
| 5 or 20 mg/m$^3$, (7 h/d) during major period of organogenesis) | No teratogenicity noted | Murray et al. 1979. IN NIOSH 1981 |
| SPECIES: Mouse | | |
| 5 or 20 mg/m$^3$, (7 h/d) during major period of organogenesis) | No teratogenicity noted | Murray et al. 1979. IN NIOSH 1981 |
| SPECIES: Chicken Eggs | | |
| 6.5 mg/m$^3$ (14 d) 0.2 to 0.3 MMD | Embryonic weights significantly reduced ($P < 0.05$), but survival rate and organ/body weight ratios for heart, liver and spleen were not. Serum lactic dehydrogenase activity of surviving embryos was significantly reduced. Hematocrit values normal | Hoffman and Campbell 1977. IN NIOSH 1981 |

## 7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

### 7.5.1 Inhalation.

1. Coughing, sneezing, tickling in nose and throat.
2. Rhinorrhea (USDHEW 1977).
3. Reflex increase in respiratory rate, and diminution of depth (NIOSH 1974).
4. Lacrimation (USDHEW 1977).
5. Conjunctivitis (USDHEW 1977).
6. Changes in mucociliary function (Newhouse et al. IN NIOSH 1981).
7. Epitaxis (USDHEW 1977).
8. Various lesions of the skin (Doc. TLV 1981)
9. Mouth becomes sore (NIOSH/OSHA 1981).
10. Mild to severe erosion of dental enamel and loss of tooth substance (USDHEW 1977).
11. Teeth may become sensitive to temperature extremes (NIOSH 1974).
12. Discolouration of teeth (Proctor 1978).
13. Inflammation of upper respiratory tract (Sax 1979).
14. Frequent respiratory infections (USDHEW 1977).
15. Tracheobronchitis (Doc. TLV 1981).
16. Residual bronchiectasis (NIOSH 1974).
17. Chronic bronchitis (Sax 1979).
18. Pulmonary fibrosis (NIOSH 1974).
19. Emphysema (USDHEW 1977).
20. Chemical pneumonitis.
21. A single overexposure may cause laryngeal, tracheobronchial and pulmonary edema (USDHEW 1977).
22. Acclimatization to subjective effects of inhalation may occur (NIOSH 1974).
23. Sensitization to the effects of sulphuric acid may occur (NIOSH 1974).

### 7.5.2 Ingestion.

1. Brown staining of teeth (AAR 1981).
2. Mucous membrane burns, circumoral burns (Sax 1979).
3. Inability to swallow, or pain upon swallowing (ITII 1981).

4. Abdominal pain (ITII 1981).
5. Stomatitis (Doc. TLV 1981).
6. Digestive disturbances (USDHEW 1977).
7. Respiratory distress (secondar to epiglottal edema) (Sax 1979).
8. Hematemesis (ITII 1981).
9. Perforation of gastrointestinal tract (AAR 1981).
10. Residual sequelae include gastrointestinal scarring and strictures (Sax 1979).
11. Shock (Sax 1979).
12. Albumin, blood and casts in urine (AAR 1981).
13. Anuria (AAR 1981).
14. Renal failure (Sax 1979).
15. Death (GE 1980).

### 7.5.3 Skin Contact.

1. Repeated contact with dilute solutions may cause dermatitis (NIOSH 1974).
2. Acid burns of eyelids and surrounding parts of face will produce cicatrization (NIOSH 1974).
3. In concentrated form, destruction of epidermis and subcutaneous tissue causing necrosis, charring, burning of skin (Sax 1979).
4. Ulceration.
5. If large area of skin exposed, shock, collapse and symptoms similar to those seen in severe burn cases (Sax 1979).
6. Pulmonary edema from inhalation of the liquid and subsequent pulmonary fibrosis, residual bronchitis and pulmonary emphysema when sprayed with fuming sulphuric acid (Goldman and Hill 1953. IN NIOSH 1974).

### 7.5.4 Eye Contact.

1. Burning sensation in eyelids and eyes, with ulceration of the tissues (Lefèvre 1980).
2. Corneal necrosis (AAR 1981).
3. Blindness (concentrated acid) (NIOSH/OSHA 1981).

## 7.6 Human Toxicity to Decay or Combustion Products

Sulphuric acid is not flammable in fire (AAR 1981). On reaction, it may evolve flammable hydrogen (AAR 1981). Sulphur oxides can result from decomposition and from oxidizing reactions of sulphuric acid (GE 1980). Toxic gases and vapours (such as

sulphuric acid fume and sulphur dioxide) may be released when sulphuric acid decomposes (NIOSH/OSHA 1981).

**7.6.1 Hydrogen and Sulphur Dioxide.** Hydrogen is a colourless, tasteless, odourless gas which when mixed with air forms explosive mixtures. With an ignition source, the air-gas mixture burns with a very hot, nonluminous flame (i.e. difficult to see).

In the absence of air and other oxidizing materials, hydrogen acts as an asphyxiant by displacing air. Persons breathing an oxygen-deficient atmosphere (< 18 percent oxygen) become cyanotic, suffer impaired alertness and muscular coordination, followed by collapse and death if exposure is prolonged. No TLV® for hydrogen is given (Doc. TLV 1981).

Sulphur dioxide is a colourless, nonflammable gas with a strong suffocating odour. It is extremely irritating to the eyes and respiratory tract (Merck 1976). The irritation of the mucous membranes probably results from the action of sulphurous acid formed when the highly soluble gas dissolves. Short-term exposure causes bronchoconstriction. The magnitude of the response is dose-related. The TLV® for sulphur dioxide is 2 ppm (8 h-TWA) and 5 ppm (STEL) (Doc. TLV 1981).

# 8 CHEMICAL COMPATIBILITY

## 8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| GENERAL | | | | | | | | | | | | | | |
| Water | • | | | | | | • | | | • | | | | Bretherick 1979 |
| Heat | | | | | • | | | | | | | | | Sax 1979 |
| SPECIFIC CHEMICALS | | | | | | | | | | | | | | |
| Acetaldehyde | | | | • | | | | | | | | | | Bretherick 1979 |
| Acetic Anhydride | • | | | | | | • | | | | | | | NFPA 1978 |
| Acetone Cyanhydrin | | • | | | | | • | | | | | | | NFPA 1978 |
| Acetonitrile | • | | | | | | • | | | | | | | NFPA 1978 |
| Acrolein | • | | | | | | • | | | | | | | NFPA 1978 |
| Acrylonitrile | | | | | | | | | | • | | | May yield unstable mixture | Bretherick 1979 |
| Allyl Alcohol | • | | | | | | • | | | | | | | NFPA 1978 |
| Allyl Chloride | • | | | • | | | • | | | | | | | NFPA 1978 |
| 2-Aminoethanol | • | | | | | | • | | | | | | | NFPA 1978 |
| Aqueous Ammonia | • | | | | | | • | | | | | | | NFPA 1978 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ammonium Iron (III) Sulphate Dodecahydrate | • | | • | | | | | | | | | | | Bretherick 1979 |
| Ammonium Triperchromate | | | • | | | | • | | | | | | | NFPA 1978 |
| Aniline | • | | | | | | • | | | | | | | NFPA 1978 |
| Benzyl Alcohol | | | • | | | • | | | | | | | | Bretherick 1979 |
| Bromine Pentafluoride | | • | | | | | | | | • | | | | Bretherick 1979 |
| n-Butyraldehyde | • | | | | | | • | | | | | | | NFPA 1978 |
| Cesium Acetylene Carbide | | • | | | | | | | | | | | Burns in sulphuric acid | NFPA 1978 |
| Chlorine Trifluoride | | | | | | | | | | • | | | | NFPA 1978 |
| 1-Chloro-2,3-epoxypropane | | | | | | | | | | • | | | | Bretherick 1979 |
| Chlorosulphonic Acid | • | | | | | | • | | | | | | | NFPA 1978 |
| Copper | | | | | | • | | | | | | | Forms sulphur dioxide | Bretherick 1979 |
| Cuprous Nitride | | | | | | | | | | • | | | | NFPA 1978 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Cyano-2-propanol | • | | | | | | • | | | • | | | | Bretherick 1979 |
| Cyclopentadiene | | • | • | | | | | | | • | | | | Bretherick 1979 |
| Cyclopentanone Oxime | | | | | | | | | | • | | | Causes eruptions | Bretherick 1979 |
| 1,3-Diazido-benzene | | • | • | | | | | | | | | | Mild explosion | Bretherick 1979 |
| Diisobutylene | • | | | | | | • | | | | | | | NFPA 1978 |
| p-Dimethylamino-benzaldehyde | • | | • | | | | | | | | | | | Bretherick 1979 |
| Epichlorohydrin | | | | | | | | | | • | | | | NFPA 1978 |
| Ethylene Cyanohydrin | | | | | | | | | | • | | | | NFPA 1978 |
| Ethylene Diamine | • | | | | | | • | | | | | | | NFPA 1978 |
| Ethylene Glycol | • | | | | | | • | | | | | | | NFPA 1978 |
| Ethylenimine | • | | | | | | • | | | | | | | NFPA 1978 |
| Hexalithium disilicide | | • | | | | | | | | | | | Incandesces and yields silicon hydrides which ignite | Bretherick 1979 |
| Hydrochloric Acid | • | | | | | | • | | | | | | | NFPA 1978 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hydrofluoric Acid | • | | | | | | • | | | | | | | NFPA 1978 |
| Hydrogen Peroxide | | | • | | | | | | | | | | Loud but non-shattering explosion | Bretherick 1979 |
| Isoprene | • | | | | | | • | | | | | | | NFPA 1978 |
| Mercuric Nitride | | | • | | | | | | | | | | | NFPA 1978 |
| Mesityl Oxide | • | | | | | | • | | | | | | | NFPA 1978 |
| Nitrobenzene | | | • | • | | | | | | | | | Yields hydrogen if acid is added to nitro-benzene | Bretherick 1979 |
| *m*-Nitrobenzene-sulphonic Acid | • | | • | | | | | | | | | | | Bretherick 1979 |
| Nitromethane | | • | • | | | | | | | | | | Susceptible to initiation by a detonator | Bretherick 1979 |
| N-Nitromethyl-amine | | | • | | • | | | | | | | | | Bretherick 1979 |
| *p*-Nitrotoluene | | | | | • | | | | | • | | | | Bretherick 1979 |
| Pentasilver Trihydroxydiamido-phosphate | | | • | | | | | | | | | | | NFPA 1978 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phosphorus | | • | | | | | | | | | | | | Bretherick 1979 |
| Phosphorous Isocyanate | | | | | | | | | | • | | | | NFPA 1978 |
| Potassium | | | • | | | | | | | | | | | Bretherick 1979 |
| Potassium t-Butoxide | | • | | | | | | | | | | | | NFPA 1978 |
| Potassium Chlorate | | • | • | | | | | | | | | | | NFPA 1978 |
| Potassium Permanganate | | | • | | | | | | | | | | | NFPA 1978 |
| β-Propiolactone | • | | | | | | • | | | | | | | NFPA 1978 |
| Propylene Oxide | • | | | | | | • | | | | | | | NFPA 1978 |
| Pyridine | • | | | | | | • | | | | | | | NFPA 1978 |
| Rubidium Acetylene Carbide | | • | | | | | | | | | | | Burns with sulphuric acid | NFPA 1978 |
| Sodium | | | • | | | | | | | | | | Anhydrous acids react slowly, while aqueous acids react explosively | Bretherick 1979 |
| Sodium Carbonate | | | | | | | | | | • | | | | NFPA 1978 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sodium Chlorate | | • | • | | | | | | | | | | | NFPA 1978 |
| Sodium Hydroxide | • | | | | | | • | | | • | | | | NFPA 1978 |
| Styrene Monomer | • | | | | | | • | | | | | | | NFPA 1978 |
| Vinyl Acetate | • | | | | | | • | | | | | | | NFPA 1978 |
| Zinc Chlorate | | • | • | | | | | | | | | | | NFPA 1978 |
| Zinc Iodide | | | | | | | | | | • | | | | Bretherick 1979 |
| CHEMICAL GROUPS | | | | | | | | | | | | | | |
| Metalacetylides or Carbides | | • | | | | | | | | | | | | Bretherick 1979 |
| Organic Acids | • | | | | | • | | | | | | | | EPA-600/2-80-076 |
| Alcohols & Glycols | • | | | | | • | | | | | | | | EPA-600/2-80-076 |
| Aldehydes | • | | | | | • | | | | | | | | EPA-600/2-80-076 |
| Amides | • | | | | | • | | | | | | | Forms nitrogen oxides | EPS-600/2-80-076 |
| Amines | • | | | | | • | | | | | | | Forms nitrogen oxide | EPA-600/2-80-076 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Azo Compounds | • | | • | | | • | • | | | | Evolves nitrogen or nitrogen oxide. Can decompose explosively | EPA-600/2-80-076 |
| Carbamates | • | | | | | • | | | | | Can generate nitrogen and sulphur oxides | EPA-600/2-80-076 |
| Caustics | • | | | | | | | | • | | | EPA-600/2-80-076 |
| Cyanides | | | • | | | • | | | | | | EPA-600/2-80-076 |
| Dithiocarbamates | • | • | | • | | • | | | | | Evolves carbon disulphide which may be ignited by the heat of decomposition | EPA-600/2-80-076 |
| Esters | • | • | | | | • | | | | | Ignition of more flammable esters may occur | EPA-600/2-80-076 |
| Ethers | • | • | | | | | | | | | Heat generated from oxidation may ignite more flammable ethers | EPA-600/2-80-076 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups** (Cont'd)

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fluorides | • | | | | | • | | | | | | | Can evolve hydrogen fluoride which is toxic and corrosive | EPA-600/2-80-076 |
| Aromatic Hydrocarbons | • | • | | | | | | | | | | | May generate sufficient heat to ignite the mixture | EPA-600/2-80-076 |
| Halogenated Organics | • | | | | • | • | | | | | | | Can give off hydrogen chloride and phosgene | EPA-600/2-80-076 |
| Isocyanates | • | | | | | • | | | | | | | Yields carbon dioxide or nitrogen oxides | EPA-600/2-80-076 |
| Ketones | • | • | | | | • | | | | | | | | EPA-600/2-80-076 |
| Mercaptans | • | | | • | | • | | | | | | | Can form hydrogen sulphide or sulphur dioxide | EPA-600/2-80-076 |
| Alkali and Alkaline Earth Metals | | • | • | • | | | | | | • | | | Hydrogen gas can be generated on contact | EPA-600/2-80-076 |
| Metals | • | | | • | | | | | | | | | Evolves hydrogen | EPA-600/2-80-076 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups** (Cont'd)

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nitrides | • | | • | | | | | | | | • | | Generates ammonia gas | EPA-600/2-80-076 |
| Nitriles | • | | | | | • | | | | | | | | EPA-600/2-80-076 |
| Nitro Compounds | • | | | | | • | | | | | • | | Produces nitrogen oxide | EPA-600/2-80-076 |
| Nitroaryl Bases | | | | | | | | • | | | • | | | Bretherick 1979 |
| Unsaturated Aliphatics | • | • | | | | | | | | | | | | EPA-600/2-80-076 |
| Saturated Aliphatics | • | | | | | | | | | | | | Yields carbon dioxide | EPA-600/2-80-076 |
| Organic Peroxides | • | | • | | | • | | | | | | | | EPA-600/2-80-076 |
| Phenols and Cresols | • | | | | | | | | | | | | | EPA-600/2-80-076 |
| Organophosphates | • | | | | | • | | | | | | | | EPA-600/2-80-076 |
| Permanganates | | | • | | | | | | | | | | | Bretherick 1979 |
| Sulphides | | | | • | | • | | | | | • | | Can form hydrogen sulphide or sulphur dioxide | Bretherick 1979 |

**8.1 Compatibility of Sulphuric Acid With Other Chemicals and Chemical Groups (Cont'd)**

| SPECIFIC CHEMICAL OR CHEMICAL GROUP | HEAT GENERATION | FIRE | EXPLOSION | FORMATION OF FLAMMABLE GASES | VIOLENT POLYMERIZATION | DECOMPOSITION | FORMATION OF TOXIC FUMES | FORMATION OF SUBSTANCES OF GREATER TOXICITY | PRESSURIZATION IN CLOSED VESSELS | SOLUBILIZATION | VIOLENT REACTION | NON-HAZARDOUS REACTION | SPECIFICS | REFERENCE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Epoxides | • | • | | | • | | | | | | | | | EPA-600/2-80-076 |
| Combustible Materials | • | • | | | | • | • | | | | | | | EPA-600/2-80-076 |
| Explosives | • | | • | | | | | | | | | | | EPA-600/2-80-076 |
| Polymerizable Compounds | • | | | | • | | • | | | | | | | EPA-600/2-80-076 |
| Reducing Agents | • | • | • | | | | | | | • | | | | EPA-600/2-80-076 |

## 8.2 Compatibility of Oleum with Other Chemicals and Chemical Groups

The compatibility of oleum with various materials is expected to be similar to sulphuric acid as indicated in the previous Section. In addition, the following data were obtained.

A temperature increase and pressurization of closed vessels occurs when oleum is mixed with acetic acid, acetic anhydride, acetonitrile, acrolein, acrylic acid, acrylonitrile, allylalcohol, allyl chloride, 2-aminoethanol, ammonia (aqueous), aniline, n-butyraldehyde, cresol, cumene, dichloroethyl ether, diethylene glycol monomethyl ether, diisobutylene, epichlorohydrin, ethyl acetate, ethylene cyanohydrin, ethylene diamine, ethylene glycol, ethyleneimine, glyoxal, hydrochloric acid, hydrofluoric acid, isoprene, isopropyl alcohol, tresityl oxide, methyl ethyl ketone, nitric acid, 2-nitropropane, β-propiolactone, propylene oxide, pyridine, sodium hydroxide, styrene, sulpholane, vinyl acetate, or vinylidene chloride (NFPA 1978) which may cause an explosion hazard (Sax 1979).

# 9 COUNTERMEASURES

## 9.1 Recommended Handling Procedures

The following procedures have been derived from a review of information found in the literature. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. These procedures should not be considered as Environment Canada's recommendations.

**9.1.1 Fire Concerns.** Sulphuric acid is a nonflammable liquid. In the concentrated form, it may cause combustible materials to ignite on contact. It reacts violently with water resulting in splattering, evolution of heat and release of an irritant mist. Contact with some metals can generate explosive hydrogen gas (GE 1980; NFPA 1978). Sulphur oxides can result from decomposition and from oxidizing reactions of sulphuric acid (GE 1980).

**9.1.2 Fire Extinguishing Agents.** Use water spray to cool containers involved in a fire to help prevent rupture (GE 1980).

Small fires: Dry chemical or $CO_2$.

Large fires: Water spray or fog.

Move containers from fire area if this can be done without risk (ERG 1980). Do not get water inside containers (EAG 1978).

**9.1.3 Evacuation.** The following are evacuation distances which appear in the literature for oleum, based on prevailing winds of 10 to 19 km/h (EAG 1978). Important parameters such as spill quantity, concentration level to which evacuation is suggested, and environmental conditions, may not be defined. Readers are advised to evaluate the use of these values with those derived from the methods to calculate hazard zones in Section 5.3 of this manual, which uses the above data.

| Approximate Size of Spill | Distance to Evacuate from Immediate Danger Area | For Maximum Safety Downwind Evacuation Area Should Be |
|---|---|---|
| 20 $m^2$ | 170 m (222 paces) | 1,620 m long, 810 m wide |
| 35 $m^2$ | 245 m (322 paces) | 2,430 m long, 1,620 m wide |
| 55 $m^2$ | 295 m (398 paces) | 3,240 m long, 1,620 m wide |
| 75 $m^2$ | 355 m (465 paces) | 3,240 m long, 1,620 m wide |

In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions.

**9.1.4 Spill Actions.**

**9.1.4.1 General.** Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (GE 1980).

Vapour suppression and/or containment of sulphuric acid or oleum spills may be accomplished by using the following recommended materials (Braley 1982): polycarbonate, anhydrous sodium sulphate, polyacrylamide, polymethyl methacrylate, silicone oil, expanded perlite and sulphonated oil.

**9.1.4.2 Spills on land.** For small spills, cover the contaminated area with sodium bicarbonate or a mixture of soda ash/slaked lime (50/50) and mix. Shovel the neutralized residues into containers for disposal. If neutralizing agent is not available, cover the area with sand or earth to absorb the liquid and shovel into containers for disposal (GE 1980; Ashland MSDS 1977). Difficulty may be encountered in neutralizing large spills with solid agents unless a good means of mixing is available. The addition of neutralizing solutions or slurries may be considered (CCPA 1982).

For large spills, contain if possible by forming dykes or use of lagoons. Pump liquid in salvage tank for recovery. The remaining liquid can be neutralized with sodium bicarbonate or soda ash/slaked lime mixture or absorbed on sand or earth. The residue can then be shoveled into containers for disposal (GE 1980; Ashland MSDS 1977).

Application of fly ash or cement powder to absorb the liquid bulk should also be considered (EPA 670/2-75-042). Sorbents such as activated carbon, Dowex, Amberlite, DeSal Process mixture and Universal Sorbent Material (USM) may also be used (CG-D-38-76).

**9.1.5 Cleanup and Treatment.**

**9.1.5.1 Spills in water.** Sodium bicarbonate is recommended as an *in situ* neutralizing agent to avoid overdosing, resulting in too great a pH increase as well as the lower heat of reaction (CG-D-16-77). Other treating agents that may be considered for neutralization are: calcined dolomite (where overrun of alkali can be tolerated), calcium oxide (where overrun of alkali can be tolerated), calcium hydroxide (where gypsum forms and slows neutralization), and sodium carbonate (where Ca and Mg content are to be kept low) (CG-D-38-76).

**9.1.5.2 General.** For treatment of contaminated water, gravity separation of solids followed by neutralization with a mixture of soda ash and lime (50/50) is recommended. Care should be taken not to create a violent reaction by fast base addition (EPA 600/2-77-227).

**9.1.6 Disposal.** Waste sulphuric acid must never be discharged directly into sewers or surface waters. Following neutralization either at the spill site or at a waste management facility, the resultant sludge can be disposed of at a secure landfill.

**9.1.7 Protective Measures.** For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be sulphuric acid:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate clothing necessary to prevent any possibility of repeated or prolonged skin contact with liquid sulphuric acid or its solutions (NIOSH/OSHA 1981).
- Close fitting, "mono goggles" type of safety glasses with plastic frames are recommended where splashing in the eyes may occur (CIL). Splash-proof or chemical safety goggles should also be considered (GE 1980; NIOSH/OSHA 1981).
- Rubber gloves, aprons, boots and suits are recommended to avoid body contact with this acid (GE 1980). Gauntlet-type, acid resistant gloves may also be used (CIL).
- PVC has been recommended as a chemical suit material (good resistance) for protection against sulphuric acid (EE-20). Vinyl has also been recommended as a suitable material (CCPA 1982).
- Nonimpervious clothing which becomes contaminated with sulphuric acid should be removed immediately and not reworn until the sulphuric acid is removed from the clothing (NIOSH/OSHA 1981).
- Eyewash fountains and safety showers with deluge type heads should be readily available to areas of use and spill situations (GE 1980).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where sulphuric acid is present (NIOSH/OSHA 1981).

| Condition | Minimum Respiratory Protection* Required Above 1 $mg/m^3$ |
|---|---|
| Particulate concentration 50 $mg/m^3$ or less | A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter. |
| | A high efficiency particulate filter respirator with a full facepiece. |
| | Any supplied-air respirator with a full facepiece, helmet, or hood. |
| | Any self-contained breathing apparatus with a full facepiece. |
| 100 $mg/m^3$ or less | A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in a continuous-flow mode. |
| Greater than 100 $mg/m^3$ or entry and escape from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. |
| | A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode. |
| Fire Fighting | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. |
| Escape | A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter.<br>Any escape self-contained breathing apparatus. |

*Only NIOSH-approved or OSHA-approved equipment should be used.

**9.1.8 Special Precautions.** Sulphuric acid in carboys or drums should be stored in clean, ventilated storage areas having acid-resistant floors with good drainage. Keep out

of direct sunlight; do not store above 32°C. Storage facilities should be separated from metallic powders, chromates, chlorates, nitrates, carbides, oxidizables, etc. Soda ash, sand or lime should be kept in general storage or work areas for emergency use. Protect containers against physical damage. Glass bottles need extra protection. Sulphuric acid is highly corrosive to most metals especially below 77 percent $H_2SO_4$. Do not add water to concentrated acid. Use nonsparking tools and vapour-proof type electrical fixtures (GE 1980).

## 9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

| | |
|---|---|
| Leak Plugging: | Plug N'Dike™ |
| Land Containment: | Bentonite Soil Sealants |
| Temporary Storage: | Portable Collection Bag System |
| Treating Agents: | Hazorb (sorbent) |

# 10 PREVIOUS SPILL EXPERIENCE

## 10.1 Tanker Truck Spill (PC SE 1982; Summary Report 1981)

A tanker truck carrying approximately 18,000 kg of concentrated sulphuric acid overturned and spilled about 95 percent of its contents off a roadway. An area of approximately 1,150 $m^2$ (230 m long by 5 m wide) was contaminated by the spill. No environmental hazards were suspected due to the frozen ground conditions at that time of year and the area being remote to family dwellings. A nearby creek was not affected.

Response crews arrived at the spill site, wearing PVC acid suits, rubber boots and gloves, but no respiratory protection. Lime was shipped to the site and applied over the contaminated area. The surface material was then excavated and hauled to a nearby landfill site. Soil samples were taken in the excavated area; the test results showed some residual acid concentrations in the soil.

Additional lime was applied to the area and mixed with the soil. More than 300 bags (45 kg/bag) of lime were used during cleanup procedures. The soil was then excavated to a depth of 1 m and hauled away to a nearby construction site, where it was incorporated into the road bed construction. The spill site was backfilled with clean soil.

## 10.2 Storage Tank Spill (PC EPS 1982; PC MWC 1982)

A storage tank, holding 92% sulphuric acid solution, started to leak its contents when the steel plug at the bottom of the tank corroded and the acid dissolved the flange. Approximately 10,000 L of sulphuric acid spilled on the ground. Company personnel dug two holes, about 1.5 m deep and 1.8 m across, to contain the acid. No remedial action was taken for 2 days due to a long holiday weekend.

On the third day, cleanup crews arrived at the spill site. Lime was carefully added on the perimeter of the holes, to partially neutralize the acid and to form an inner liner to prevent seepage. The acid was pumped into a tank and further neutralized with additional lime to pH 7.0. The resultant sludge was disposed of into a nearby landfill. The contaminated soil was then dug to a depth of about 0.5 m, mixed with lime and finally graded to its original surface condition. Approximately 12,000 kg of lime were used during cleanup and treatment.

No environmental effects resulted from the spill. The heavy clay soil in the area prevented the acid from migrating further underground. It should be noted, however, that the company where the spill occurred was neither prepared nor equipped to handle such a spill.

# 11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analyses of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g. commonly used industrial methods) were found, they have been presented as well.

## 11.1 Quantitative Methods for the Detection of Sulphuric Acid in Air

**11.1.1 Titration** (NIOSH 1974). This method may be used to determine from 0.561 to 2.577 mg/m$^3$ (0.14 to 0.64 ppm) sulphuric acid in air. The precision is $\pm$0.082 mg/m$^3$ for this method.

A filter unit consisting of a mixed cellulose ester membrane filter, 0.8 µm pore size and 37 mm diameter, held in place by a cellulose backup pad in a polystyrene 37 mm three-piece cassette filter holder is used. A sample of 180 L is collected at a rate of 1.5 L/min. The filter must be placed in a clean screw cap bottle within 1 hour of collection. The filter is extracted with isopropyl alcohol which is then titrated with barium perchlorate using thorin as the indicator. Most metal ions interfere by forming coloured complexes with the thorin indicator. There is an advantage to this method in that the sampling device is small, portable and involves no liquids. The titration is rapid and simple. The method does not distinguish between sulphuric acid and other sulphates. Acidity should also be measured to determine the fraction of sulphate that is in the acid form.

Alternately, sodium hydroxide is used for titration (Patton 1963). The indicators used are either bromophenol blue or phenolphthalein. The method is simple,

direct and easy but is not specific for sulphuric acid. It assumes that there are no other acids or bases present.

**11.1.2 Ion Chromatography** (Hussar 1978). Concentrations as low as 0.02 µg/mL sulphate in the extracting solution may be determined.

Samples are collected using dichotomous samplers. The filters are extracted with perchloric acid using ultrasound. A 5 mL aliquot of the extract is spiked with a 1:1 mixture of standard eluent. This eluent contains 0.003 M sodium bicarbonate and 0.0024 M sodium carbonate. A suitable volume is injected into an ion chromatograph. Peak areas and retention times are used to identify and quantify species of interest relative to standards. This method is useful over a wide range of concentrations.

**11.1.3 Flame Photometric Detection** (EPA-600/52-81-013). Total sulphuric acid may be determined in air at concentrations as low as 0.26 µg/m$^3$ (0.07 ppb) using a sulphuric acid analyzer equipped with a flame photometric detector.

A volume of air is drawn into the sulphuric acid analyzer and is mixed with moist air followed by hydrogen chloride gas (dilute). The sample gas is passed through a heating chamber, rapidly heated and then condensed on the walls of a collector chamber. The flame photometric detector is connected directly to the downstream side of the collector tube and receives a continuous supply of hydrogen gas (140 mL/min) and sample gas (200 mL/min). The analyzer uses hydrogen chloride to prevent contaminants such as ammonia, sulphur dioxide, and ammonium sulphates from interfering with the analysis. The method is open to further development and evaluative testing.

## 11.2 Qualitative Method for the Detection of Sulphuric Acid in Air

The sample is collected as in Section 11.1.1. A 1.0 mL volume of sample is acidified with 6 M hydrochloric acid followed by 1 mL of 1 M barium chloride solution. A finely divided white precipitate indicates the presence of the sulphate ion (Welcher 1955).

## 11.3 Quantitative Methods for the Detection of Sulphuric Acid in Water

**11.3.1 Gravimetric** (ASTM 1979; AWWA 1976). The range of concentrations which can be analyzed gravimetrically is 20 to 100 ppm sulphate in water. This may be adapted to higher or lower ranges depending on sample size. Precision is $\pm$ 1 percent. This method measures the sulphate ion; thus, other sulphates, e.g. natural gypsum, present are also measured.

The sample is filtered if it is turbid. The pH is adjusted to the methyl orange end with 10 percent hydrochloric acid and a 10 mL excess of hydrochloric acid is added.

The solution is heated and an 11.8 percent solution of barium chloride is added until precipitation is complete. The precipitated barium sulphate is filtered, washed, and ignited to consume all the carbon. If silicon is present, concentrated hydrofluoric acid is added to expel it as $SiF_4$. The residue is re-ignited, cooled and weighed. This method is applicable to all types of water but it is tedious and time consuming. Calcium interferes with the analysis since it is strongly coprecipitated.

**11.3.2 Turbidimetric** (ASTM 1979; AWWA 1976). This method may be used to determine from 10 to 100 ppm sulphate ion in water with a precision of $\pm$ 5 percent or 2 mg/L, whichever is greater.

The sample is filtered if it is turbid and the temperature is adjusted to between 15 and 30°C. A conditioning reagent is added to stabilize the solution and remove interferences. It is prepared by mixing 50 mL glycerol with a solution containing 30 mL concentrated hydrochloric acid, 300 mL distilled water, 100 mL 95 percent ethyl or isopropyl alcohol and 75 g sodium chloride. A 100 mL sample aliquot is mixed with 5.0 mL conditioning reagent. While the solution is being stirred, barium chloride crystals are added and stirring continues for 1 minute. The sulphate ion is converted to a barium sulphate suspension. The turbidity is determined using a photoelectric colourimeter or a spectrophotometer and compared to a standard curve. Insoluble suspended matter and coloured components interfere. This method is suitable for rapid routine or control tests where extreme accuracy and precision are not required.

## 11.4 Qualitative Method for the Detection of Sulphuric Acid in Water

The sample is collected as in Section 11.3.1. A 1 mL volume of sample is acidified with 6 M hydrochloric acid. This is followed by 1 mL of 1 M barium chloride solution. A finely divided white precipitate indicates the presence of the sulphate ion (Welcher 1955).

## 11.5 Quantitative Methods for the Detection of Sulphuric Acid in Soil

**11.5.1 Ion Chromatography** (Dionex 1978). The detection limit for sulphate is 3 ppm in the lithium chloride extracting solution. The precision is $\pm$ 3 percent. As the sulphate ion is measured, this method then yields the total amount of sulphate present.

A 5 g sample of soil is collected and extracted with 0.001 M lithium chloride solution, centrifuged and filtered. The sample solution is injected into an ion chromatograph and quantitated using retention times and peak heights. The method is simple but requires specialized equipment.

**11.5.2 Gravimetric** (Hesse 1972). The range of concentrations which can be analyzed gravimetrically is 20 to 100 ppm sulphate in the extract. The size of the soil sample used for extraction may be decreased if a high concentration of sulphuric acid is present.

A soil sample of known weight is extracted with a solution of sodium acetate and acetic acid buffered to pH 4.5. One part soil is shaken with five parts extractant for 30 minutes and then centrifuged or filtered. A suitable aliquot is taken. The pH is adjusted with 1 M hydrochloric acid to the methyl orange end point and an excess of 1 mL hydrochloric acid is added. Barium chloride is added with heating and shaking. The liquid is removed and the barium sulphate precipitate dried by heating overnight at 105°C. It is cooled and weighed. This method is applicable to samples containing large amounts of sulphuric acid. The method is accurate and precise but is tedious and slow. It is not suitable for situations where the results of the analysis are needed quickly.

**11.5.3 Turbidimetric** (Hesse 1972). Concentrations of 2 to 10 ppm sulphate in the extracting solution may be analyzed using this method. The range may be varied by varying the amount of soil used.

A soil sample of known weight is extracted with a solution of sodium acetate and acetic acid buffered to pH 4.5. One part soil is shaken with five parts extractant for 30 minutes and then centrifuged or filtered. Iron (III) chloride solution is added to a suitable aliquot of soil extract. This is followed by sodium hydroxide added dropwise with shaking. The solution is filtered or centrifuged, acidified with acetic acid and diluted to volume. Barium chloride is added to a suitable aliquot of the clear extract and mixed. Gum acacia solution is added, the extract is diluted to volume and mixed. The turbidity is measured with a spectrophotometer at 490 nm or with a blue filter. The calibration curve should cover the range 0 to 10 $\mu g/cm^3$ sulphur. Calcium interferes with the analysis since calcium sulphate is coprecipitated. This method is suitable for rapid routine or control tests where extreme accuracy and precision are not required.

## 11.6 Qualitative Method for the Detection of Sulphuric Acid in Soil

One sample is collected and extracted as in Section 11.5.1. A 1 mL volume of sample is acidified with 6 M hydrochloric acid followed by 1 mL of 1 M barium chloride solution. A finely divided white precipitate indicates the presence of the sulphate ion (Welcher 1955).

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EnviroTIPS

Common Abbreviations

| | |
|---|---|
| BOD | biological oxygen demand |
| b.p. | boiling point |
| CC | closed cup |
| cm | centimetre |
| CMD | count median diameter |
| COD | chemical oxygen demand |
| conc. | concentration |
| c.t. | critical temperature |
| eV | electron volt |
| g | gram |
| ha | hectare |
| Hg | mercury |
| IDLH | immediately dangerous to life and health |
| Imp. gal. | imperial gallon |
| in. | inch |
| J | joule |
| kg | kilogram |
| kJ | kilojoule |
| km | kilometre |
| kPa | kilopascal |
| kt | kilotonne |
| L | litre |
| lb. | pound |
| $LC_{50}$ | lethal concentration fifty |
| $LC_{LO}$ | lethal concentration low |
| $LD_{50}$ | lethal dose fifty |
| $LD_{LO}$ | lethal dose low |
| LEL | lower explosive limit |
| LFL | lower flammability limit |
| m | metre |
| *m* | meta |
| M | molar |
| MAC | maximum acceptable concentration |
| max | maximum |
| mg | milligram |
| MIC | maximum immision concentration |
| min | minute or minimum |
| mm | millimetre |
| µg | microgram |
| µm | micrometre |
| °Be | degrees Baumé (density) |
| MMAD | mass median aerodynamic diameter |
| MMD | mass median diameter |
| m.p. | melting point |
| MW | molecular weight |
| N | newton |
| NAS | National Academy of Sciences |
| NFPA | National Fire Protection Association |
| NIOSH | National Institute for Occupational Safety and Health |
| nm | nanometre |
| *o* | ortho |
| OC | open cup |
| *p* | para |
| $P_c$ | critical pressure |
| PEL | permissible exposure level |
| pH | measure of acidity/alkalinity |
| ppb | parts per billion |
| ppm | parts per million |
| $P_s$ | standard pressure |
| psi | pounds per square inch |
| s | second |
| STEL | short-term exposure limit |
| STIL | short-term inhalation limit |
| $T_c$ | critical temperature |
| $TC_{LO}$ | toxic concentration low |
| $T_d$ | decomposition temperature |
| $TD_{LO}$ | toxic dose low |
| $TL_m$ | median tolerance limit |
| TLV | Threshold Limit Value |
| $T_s$ | standard temperature |
| TWA | time weighted average |
| UEL | upper explosive limit |
| UFL | upper flammability limit |
| VMD | volume mean diameter |
| v/v | volume per volume |
| w/w | weight per weight |